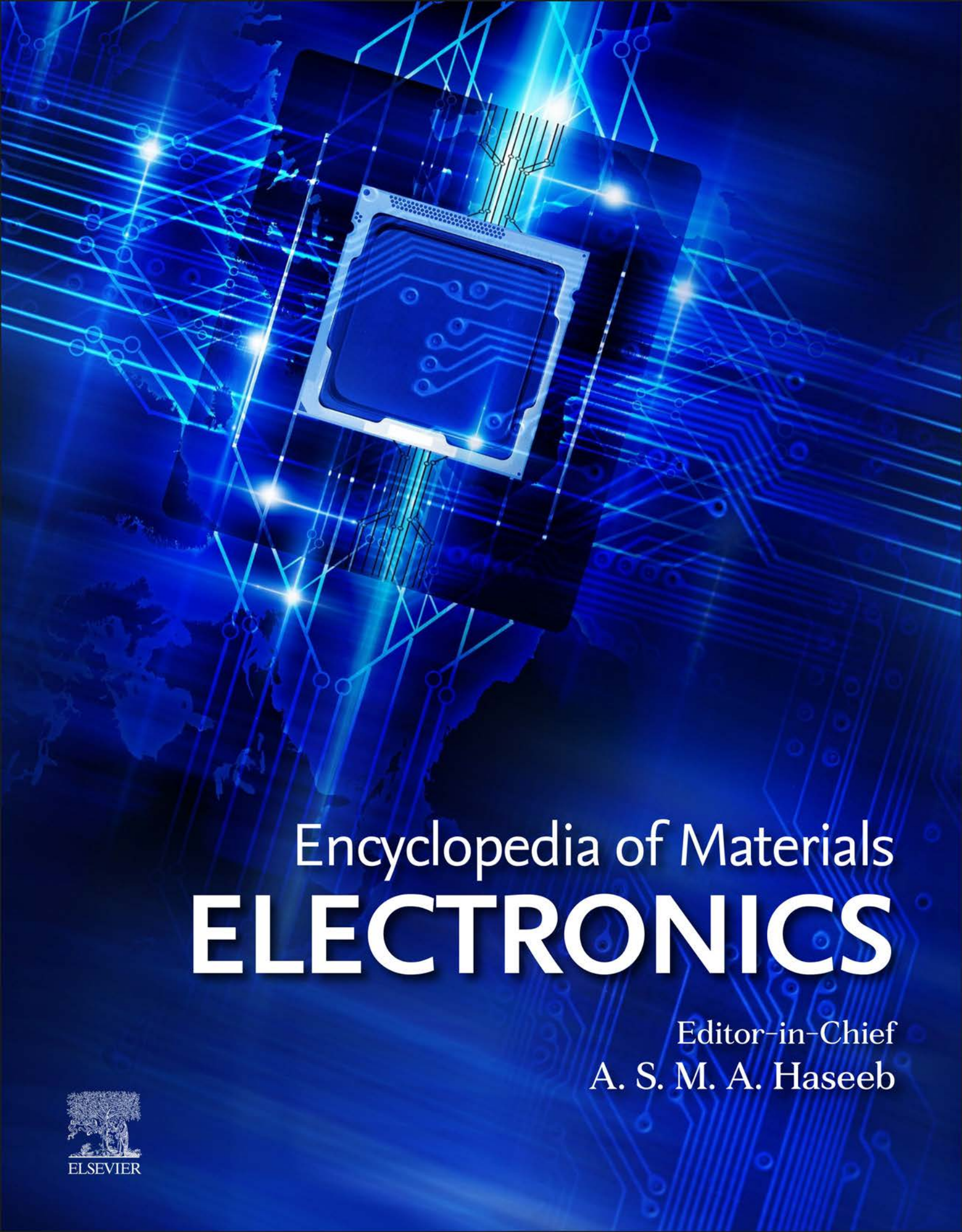




Encyclopedia of Materials **ELECTRONICS**

Editor-in-Chief
A. S. M. A. Haseeb

ENCYCLOPEDIA OF MATERIALS: ELECTRONICS

ENCYCLOPEDIA OF MATERIALS: ELECTRONICS

Editor-in-Chief

A. S. M. A. HASEEB

Department of Nanomaterials and Ceramic Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh

Volume 1

Organic Electronics, Electroceramics and Complex Oxides, and Magnetic Materials

Section Editors

Arokia Nathan

Darwin College, University of Cambridge, United Kingdom

Chen Jiang

Tsinghua University, China

DaeYong Jeong

Department of Materials Science & Engineering, Inha University, Incheon, Korea

Paolo Ghigna

Department of Chemistry, University of Pavia and National Interuniversity Consortium of Materials Science and Technology, INSTM, Pavia, Italy

Manh-Huong Phan

Professor of Physics, University of South Florida



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Designer: Christian Billow

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LIST OF CONTRIBUTORS FOR VOLUME 1

Manfred Albrecht

Institute of Physics, University of Augsburg, Augsburg, Germany

Sedat Alkoy

Department of Materials Science and Engineering, Gebze Technical University, Gebze, Kocaeli, Turkey

Ryan L. Arevalo

Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick, Ireland

Christian Binek

Department of Physics and Astronomy and Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE, United States

Juan M. Blanco

Department of Applied Physics, EIG, UPV/EHU, San Sebastian, Spain

Annalisa Bonfiglio

Department of Electrical and Electronic Engineering, University of Cagliari, Cagliari, Italy and Scuola Universitaria Superiore, IUSS - Pavia, Italy

Pietro Carretta

Department of Physics, University of Pavia, Pavia, Italy

Amit Chanda

Department of Physics, University of South Florida, Tampa, FL, United States

Thitirat Charoonsuk

Advanced Materials Research Unit, Department of Chemistry, School of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand and Department of Materials Science, Srinakharinwirot University, Bangkok, Thailand

Ning Chen

College of Materials Science and Engineering, Sichuan University, Chengdu, China

Pan Chen

School of Energy Engineering, Huanghuai University, Zhumadian, China and Henan International Joint Laboratory of Structural Mechanics and Computational Simulation, Huanghuai University, Zhumadian, China

Yuan Cheng

College of Materials Science and Engineering, Sichuan University, Chengdu, China

Hamid T. Chorsi

University of California Santa Barbara, Santa Barbara, CA, United States

Meysam T. Chorsi

University of Connecticut, CT, United States

Baojin Chu

CAS Key Laboratory of Materials for Energy Conversion and Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, China

Ta-Ya Chu

Advanced Electronics and Photonics Research Centre, National Research Council Canada, Ottawa, ON, Canada

Elisabetta Comini

Sensor Laboratory, Department of Information Engineering, University of Brescia, Brescia, Italy

Paula Corte-Leon

Department Advanced Polymers and Materials: Physics, Chemistry and Technology, Faculty of Chemistry, UPV/EHU, San Sebastian, Spain

Piero Cosseddu

Department of Electrical and Electronic Engineering, University of Cagliari, Cagliari, Italy

Navneet Dabra

Department of Sciences, Mata Sahib Kaur Girls College, Talwandi Sabo, Bathinda, Punjab, India

Ngoc-Toan Dang

Institute of Research and Development and Faculty Environmental of Natural Sciences, Duy Tan University, Danang, Vietnam

Mangal Das

Indian Institute of Technology Indore, Simrol, Indore, India

Ritopa Das

University of Connecticut, CT, United States

Ulrike Diebold

Institute of Applied Physics, TU Wien, Vienna, Austria

Álvaro Díaz-García

Department of Condensed Matter Physics, ICMS-CSIC, University of Sevilla, Sevilla, Spain

Takashi Eshita

Wakayama University, Wakayama, Japan

Diana Estevez

Institute for Composites Science Innovation, School of Materials Science and Engineering, Zhejiang University, Hangzhou, PR China

Giada Franceschi

Institute of Applied Physics, TU Wien, Vienna, Austria

Victorino Franco

Department of Condensed Matter Physics, ICMS-CSIC, University of Sevilla, Sevilla, Spain

Tarun Garg

Yadavindra Department of Sciences, Punjabi University Guru Kashi, Talwandi Sabo, Bathinda, Punjab, India

Paolo Ghigna

Department of Chemistry, University of Pavia, Pavia, Italy

Xiaojun Guo

Department of Electronic Engineering Shanghai Jiao Tong University, Shanghai, China

Horst Hahn

KIT-TUD Joint Research Laboratory Nanomaterials – Technical University of Darmstadt, Darmstadt, Germany; Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany; and School of Chemical, Biological and Materials Engineering, The University of Oklahoma, Norman, OK, United States

Nguyen Hoang Hai

Nano and Energy Center, University of Science, Vietnam National University, Hanoi, Vietnam

Lei Han

Department of Electronic Engineering Shanghai Jiao Tong University, Shanghai, China

A.S.M.A. Haseeb

Department of Nanomaterials and Ceramic Engineering (NCE), Bangladesh University of Engineering and Technology (BUET), Dhaka

Tobias Hemsell

Faculty of Mechanical Engineering, Dynamics and Mechatronics, Paderborn University, Paderborn, Germany

Stefan Hengsbach

Karlsruhe Institute of Technology, Institute of Microstructure Technology, Eggenstein-Leopoldshafen, Germany

Yukinobu Hikosaka

Fujitsu Semiconductor Memory Solution Limited, Fukushima, Japan

Atsufumi Hirohata

Department of Electronic Engineering, University of York, York, United Kingdom

Christian Holzmann

Institute of Physics, University of Augsburg, Augsburg, Germany

Wenping Hu

Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Department of Chemistry, School of Science, Tianjin University & Collaborative Innovation Center of Chemical Science and Engineering, Tianjin, China.

Jia Huang

Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Shanghai Institute of Intelligent Science and Technology, Tongji University, Shanghai, PR China

Jasbir S. Hundal

Punjabi University Guru Kashi, Talwandi Sabo, Bathinda, Punjab, India

Chang-Ming Hung

Department of Physics, University of South Florida, Tampa, FL, United States

Horea Ilies

University of Connecticut, CT, United States

Mihail Ipatov

Department Advanced Polymers and Materials: Physics, Chemistry and Technology, Faculty of Chemistry, UPV/EHU, San Sebastian, Spain

Monsur Islam

Karlsruhe Institute of Technology, Institute of Microstructure Technology, Eggenstein-Leopoldshafen, Germany

Dae-Yong Jeong

Department of Materials Science & Engineering, Inha University, Incheon, South Korea

DaeYong Jeong

Department of Materials Science and Engineering, Inha University, Incheon, Republic of Korea

Chen Jiang

Department of Electronic Engineering, Tsinghua University, Beijing, China

Hyun Suk Jung

School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Korea

Vijay S. Kalappattil

Department of Physics, Colorado State University, Fort Collins, CO, United States

Maths Karlsson
*Department of Chemistry and Chemical Engineering,
 Chalmers University of Technology, Göteborg, Sweden*

Kazem Kazerounian
University of Connecticut, CT, United States

Hyouon Woo Kim
*The Research Institute of Industrial Science and Division
 of Materials Science and Engineering Hanyang
 University, Seoul, Republic of Korea*

Sang Sub Kim
*Department of Materials Science and Engineering, Inha
 University, Incheon, Republic of Korea*

Jan G. Korvink
*Karlsruhe Institute of Technology, Institute of
 Microstructure Technology, Eggenstein-Leopoldshafen,
 Germany*

Denis P. Kozlenko
*Frank Laboratory of Neutron Physics, Joint Institute for
 Nuclear Research, Dubna, Russia*

Robert Kruk
*Institute of Nanotechnology, Karlsruhe Institute of
 Technology, Eggenstein-Leopoldshafen, Germany*

Ajeet Kumar
*School of Materials Science and Engineering, Yeungnam
 University, Gyeongsan, South Korea*

Amitesh Kumar
*Indian Institute of Technology Indore, Simrol, Indore,
 India*

Gayana W.C. Kumarage
*Sensor Laboratory, Department of Information
 Engineering, University of Brescia, Brescia, Italy*

Stefano Lai
*Department of Electrical and Electronic Engineering,
 University of Cagliari, Cagliari, Italy*

Jia Yan Law
*Department of Condensed Matter Physics, ICMS-CSIC,
 University of Sevilla, Sevilla, Spain*

Thinh T. Le
University of Connecticut, CT, United States

Keryn Lian
*Department of Materials Science and Engineering,
 University of Toronto, Toronto, ON, Canada*

Chuan Liu
*State Key Lab of Opto-Electronic Materials &
 Technologies, Guangdong Province Key Lab of Display
 Material and Technology, School of Electronics and
 Information Technology, Sun Yat-Sen University,
 Guangdong, China*

Dapeng Liu
*Interdisciplinary Materials Research Center, School of
 Materials Science and Engineering, Shanghai Institute of
 Intelligent Science and Technology, Tongji University,
 Shanghai, PR China*

Meifeng Liu
*Institute of Advanced Materials, Hubei Normal
 University, Huangshi, China*

Nguyen Hoang Luong
*Nano and Energy Center, University of Science,
 Vietnam National University, Hanoi, Vietnam*

I.B. Mısırlıoğlu
*Faculty of Natural Sciences and Engineering, Sabanci
 University, Istanbul, Turkey*

Dario Mager
*Karlsruhe Institute of Technology, Institute of
 Microstructure Technology, Eggenstein-Leopoldshafen,
 Germany*

Sanjit Manohar Majhi
*The Research Institute of Industrial Science and Division
 of Materials Science and Engineering Hanyang
 University, Seoul, Republic of Korea and Department of
 Materials Science and Engineering, Inha University,
 Incheon, Republic of Korea*

Tosapol Maluangnont
*Electroceraamics Research Laboratory, College of
 Materials Innovation and Technology, King Mongkut's
 Institute of Technology Ladkrabang, Bangkok, Thailand*

David Mandrus
*University of Tennessee, Knoxville, TN, United States
 and Oak Ridge National Laboratory, Oak Ridge, TN,
 United States*

Lluís F. Marsal
*Department of Electric Electronic and Automatic
 Engineering, Universitat Rovira i Virgili, Campus
 Sescelades, Tarragona, Spain*

Ebru Menşur-Alkoy
*Department of Materials Science and Engineering,
 Gebze Technical University, Gebze, Kocaeli, Turkey*

Ali Mirzaei
*Department of Materials Science and Engineering,
 Shiraz University of Technology, Shiraz, Iran*

Luis M. Moreno-Ramírez
*Department of Condensed Matter Physics, ICMS-CSIC,
 University of Sevilla, Sevilla, Spain*

Sk. Abdul Moyez
*Department of Chemical Engineering, University of
 Calcutta, Kolkata, India*

Shaibal Mukherjee
Indian Institute of Technology Indore, Simrol, Indore, India

Nguyen H. Nam
Nano and Energy Center, University of Science, Vietnam National University, Hanoi, Vietnam

Wanatchaporn Namhongsa
Center of Excellence on Alternative Energy, Sakon Nakhon Rajabhat University, Sakon Nakhon, Thailand

Arokia Nathan
Darwin College, University of Cambridge, Cambridge, United Kingdom

Sachin T. Navale
The Research Institute of Industrial Science and Division of Materials Science and Engineering Hanyang University, Seoul, Republic of Korea and Department of Materials Science and Engineering, Inha University, Incheon, Republic of Korea

Steffen Neitzel-Grieshammer
Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

Thanh D. Nguyen
University of Connecticut, CT, United States

M.B. Okatan
Department of Materials Science and Engineering, Izmir Institute of Technology, Izmir, Turkey

Bang Ouyang
Department of Electronic Engineering Shanghai Jiao Tong University, Shanghai, China

Alexandra F. Paterson
University of Kentucky Center for Applied Energy Research, Lexington, KY, United States

Deepak R. Patil
School of Materials Science and Engineering, Yeungnam University, Gyeongsan, South Korea

Arkashis Paul
Department of Chemical Engineering, University of Calcutta, Kolkata, India

Swastik Paul
Department of Chemical Engineering, University of Calcutta, Kolkata, India

Manh-Huong Phan
Department of Physics, University of South Florida, Tampa, FL, United States

The-Long Phan
Faculty of Engineering Physics and Nanotechnology, VNU-University of Engineering and Technology, Hanoi, Vietnam

Giacomo Prando
Department of Physics, University of Pavia, Pavia, Italy

Faxiang Qin
Institute for Composites Science Innovation, School of Materials Science and Engineering, Zhejiang University, Hangzhou, PR China

Xiaochen Ren
Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Department of Chemistry, School of Science, Tianjin University & Collaborative Innovation Center of Chemical Science and Engineering, Tianjin, China.

Subhasis Roy
Department of Chemical Engineering, University of Calcutta, Kolkata, India

Jungho Ryu
School of Materials Science and Engineering, Yeungnam University, Gyeongsan, South Korea

Abhishek Sarkar
KIT-TUD Joint Research Laboratory Nanomaterials – Technical University of Darmstadt, Darmstadt, Germany and Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

Baidurya Sarkar
Department of Chemical Engineering, University of Calcutta, Kolkata, India

Tosawat Seetawan
Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Sakon Nakhon, Thailand

Maryam Shahi
University of Kentucky Center for Applied Energy Research, Lexington, KY, United States

Denis D. Sheka
Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

Qianqian Shi
Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Shanghai Institute of Intelligent Science and Technology, Tongji University, Shanghai, PR China

Kunchit Singsoog
Center of Excellence on Alternative Energy, Sakon Nakhon Rajabhat University, Sakon Nakhon, Thailand

Atul D. Sontakke
Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, The Netherlands

Andrea Spanu
Scuola Universitaria Superiore, IUSS - Pavia, Italy

Hari Srikanth
*Department of Physics, University of South Florida,
Tampa, FL, United States*

Saichon Sriphan
*King Mongkut's University of Technology North
Bangkok, Rayong, Thailand and Advanced Materials
Research Unit, Department of Chemistry, School of
Science, King Mongkut's Institute of Technology
Ladkrabang, Bangkok, Thailand*

Huabin Sun
*College of Integrated Circuit Science and Engineering,
Nanjing University of Posts and Telecommunications,
Nanjing, China and Guangdong Greater Bay Area
Institute of Integrated Circuit and System, Guangzhou,
China*

Jia Sun
*Hunan Key Laboratory for Super Microstructure and
Ultrafast Process, School of Physics and Electronics,
Central South University, Changsha, Hunan, PR China
and Hunan Key Laboratory of Nanophotonics and
Devices, School of Physics and Electronics, Central South
University, Changsha, Hunan, PR China*

José G. Sánchez
*Institute of Chemical Research of Catalonia-The
Barcelona Institute of Science and Technology (ICIQ-
BIST), Tarragona, Spain*

Zhi Tan
*College of Materials Science and Engineering, Sichuan
University, Chengdu, China*

Manjing Tang
*College of Materials Science and Engineering, Sichuan
University, Chengdu, China*

Atul Thakre
*School of Materials Science and Engineering, Yeungnam
University, Gyeongsan, South Korea*

Dongxia Tian
*Institute of Advanced Materials, Hubei Normal
University, Huangshi, China*

Alfonsina A.A. Torim tubun
*Department of Electric Electronic and Automatic
Engineering, Universitat Rovira i Virgili, Campus
Sescelades, Tarragona, Spain*

Jens Twiefel
*Institute of Dynamics and Vibration Research, Leibniz
University Hannover, Garbsen, Germany*

Ken-ichi Uchida
*National Institute for Materials Science, Tsukuba,
Ibaraki, Japan*

K. Uchino
*Electrical Engineering, The Penn State University, State
College, PA, United States*

Kenji Uchino
*Electrical Engineering, The Penn State University,
University Park, PA, United States*

Matthias Vandichel
*Department of Chemical Sciences and Bernal Institute,
University of Limerick, Limerick, Ireland*

Tra Vinikoor
University of Connecticut, CT, United States

Naratip Vittayakorn
*Advanced Materials Research Unit, Department of
Chemistry, School of Science, King Mongkut's Institute
of Technology Ladkrabang, Bangkok, Thailand and
Department of Chemistry, School of Science, King
Mongkut's Institute of Technology Ladkrabang, Bangkok,
Thailand*

Athorn Vora-ud
*Program of Physics, Faculty of Science and Technology,
Sakon Nakhon Rajabhat University, Sakon Nakhon,
Thailand*

Guan Ying Wang
*Department of Materials Science and Engineering,
University of Toronto, Toronto, ON, Canada*

Wensheng Wang
*Fujitsu Semiconductor Memory Solution Limited,
Fukushima, Japan*

Xiuzhang Wang
*Institute of Advanced Materials, Hubei Normal
University, Huangshi, China*

Guohua Xie
*The Institute of Flexible Electronics (Future
Technologies), Xiamen University, Xiamen, PR China*

Lixu Xie
*College of Materials Science and Engineering, Sichuan
University, Chengdu, China*

Jie Xing
*College of Materials Science and Engineering, Sichuan
University, Chengdu, China*

Xiaoshan Xu
*Department of Physics and Astronomy and Nebraska
Center for Materials and Nanoscience, University of
Nebraska, Lincoln, NE, United States*

Yong Xu

*College of Integrated Circuit Science and Engineering,
Nanjing University of Posts and Telecommunications,
Nanjing, China and Guangdong Greater Bay Area
Institute of Integrated Circuit and System, Guangzhou,
China*

Qin Xue

*Department of Physical Science and Technology, Central
China Normal University, Wuhan, PR China*

Shunsuke Yamamoto

*Graduate school of Engineering, Tohoku University,
Sendai, Japan*

Zhihao Yu

*College of Integrated Circuit Science and Engineering,
Nanjing University of Posts and Telecommunications,
Nanjing, China and Guangdong Greater Bay Area
Institute of Integrated Circuit and System, Guangzhou,
China*

Bosheng Zhou

*Hunan Key Laboratory for Super Microstructure and
Ultrafast Process, School of Physics and Electronics,*

*Central South University, Changsha, Hunan, PR China
and Hunan Key Laboratory of Nanophotonics and
Devices, School of Physics and Electronics, Central South
University, Changsha, Hunan, PR China*

Jianguo Zhu

*College of Materials Science and Engineering, Sichuan
University, Chengdu, China*

Arcady P. Zhukov

*Department Advanced Polymers and Materials: Physics,
Chemistry and Technology, Faculty of Chemistry, UPV/
EHU and Department of Applied Physics, EIG, UPV/
EHU, Spain*

Valentina Zhukova

*Department Advanced Polymers and Materials: Physics,
Chemistry and Technology, Faculty of Chemistry, UPV/
EHU and Department of Applied Physics, EIG, UPV/
EHU, San Sebastian, Spain*

Editor-in-Chief

A. S. M. A. Haseeb



A. S. M. A. Haseeb received his PhD in 1992 in materials engineering from the Catholic University of Leuven (KU Leuven), Belgium. He is currently working as a professor in the Department of Nanomaterials and Ceramic Engineering (NCE), Bangladesh University of Engineering and Technology (BUET), Dhaka. Prior to joining the NCE Dept., BUET, he worked as a professor in the Department of Mechanical Engineering, University of Malaya (UM), Kuala Lumpur during Dec 2006 - June 2022. He served, during 2013-2022, as the Dean of Innovative Industry and Sustainability Research Cluster, Institute of Research Management and Monitoring, UM. His research interest includes nanostructures for gas sensing applications, electronic packaging materials and reliability and degradation of materials in hostile environment. He has authored and co-authored more than three hundred sixty research papers in peer reviewed journals and conference proceedings. Prof. Haseeb is a Fellow of the Institute of Mechanical Engineers, UK, and a Chartered Engineer, The Engineering Council, UK.

Section Editors

Arokia Nathan



Arokia Nathan is a leading pioneer in the development and application of thin film transistor technologies to flexible electronics, display and sensor systems. Following his PhD in Electrical Engineering, University of Alberta, Canada in 1988, he joined LSI Logic USA and subsequently the Institute of Quantum Electronics, ETH Zürich, Switzerland, before joining the Electrical and Computer Engineering Department, University of Waterloo, Canada. In 2006, he joined the London Centre for Nanotechnology, University College London as the Sumitomo Chair of Nanotechnology. He moved to Cambridge University in 2011 as the Chair of Photonic Systems and Displays, and he is currently a Bye-Fellow and Tutor at Darwin College. He has over 600 publications including 6 books, and more than 130 patents and four spin-off companies. He is a Fellow of IEEE, a Distinguished Lecturer of the IEEE Electron Devices Society and Sensor Council, a Chartered Engineer (UK), Fellow of the Institution of Engineering and Technology (UK), Fellow of the Royal Academy of Engineering, Fellow of the Society for Information Displays, and winner of the 2020 IEEE EDS JJ Ebers Award.

Dae Yong Jeong



Dr. Dae Yong Jeong is a professor in the Department of Materials Science and Engineering at Inha University, Korea. He was educated in Seoul National University as an undergraduate and graduate for master degree. He received Ph.D. degree from Materials at Pennsylvania State University in 2004 on Relaxor ferroelectric properties and device applications. He worked for the TRS Ind. USA and RIEC at Tohoku University, Japan. After returning to Korea, he was a senior researcher in KIST and an assistant professor at Myongji Univ. Since Sep. 2011, he is teaching and researching at Inha University. His current research interests include energy harvesting, ferroelectrics, nano-engineering for materials development, high energy density capacitor, and piezoelectric devices. Also, he has an interest in innovative Engineering Education and Intellectual properties.

Paolo Ghigna



Paolo Ghigna is Professor of Physical Chemistry at the Department of Chemistry at the University of Pavia, Italy. He holds degrees from the University of Pavia, and was a post-doctoral fellow at the University of Kent at Canterbury (UK). He is currently member of the American Chemical Society, of the Italian Chemical Society, of the Italian Association of Crystallography, of the International Society of Electrochemistry, and he has served as vice-president of SILS, the Italian Synchrotron Light Association, of which he is member. From 2000 to 2010, he acted as visiting and consultant

scientist at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). His research is focused on all the applications of Synchrotron Light to the study of matter, with emphasis on the local electronic and atomic structure of oxides, particularly in applications for energetics. He is presently involved in a number of research project for the application of operando X-ray absorption spectroscopies for the study of heterogeneous reactions, where oxides function as catalytic materials or are directly involved in the reaction.

Chen Jiang



Dr Chen Jiang is currently an assistant professor, with the Department of Electronic Engineering, Tsinghua University. He received the BS degree in engineering from the Department of Electronic Engineering, Shanghai Jiao Tong University, China, and the Ph.D. degree in Engineering from University of Cambridge, UK. From 2018 to 2021, he was supported by the Wellcome Trust as a Junior Interdisciplinary Fellow at the Department of Clinical Neurosciences, University of Cambridge, UK. His research focuses on novel electronic device architectures, large-area flexible transparent electronics, low-power circuits, and their applications to bioelectronics. Dr Jiang was a recipient of the IEEE Electron Devices Society PhD Student Fellowship 2018.

Manh-Huong Phan



Dr. Manh-Huong Phan is a Full Professor of Physics at the University of South Florida. He received a Ph.D. degree in Engineering Physics from Bristol University, UK in 2006. He is a leading expert in the development of advanced magnetocaloric and magnetoimpedance materials for energy-efficient magnetic refrigeration and smart sensor technologies, respectively. Recently, his group has discovered light-tunable room temperature ferromagnetism in atomically thin van der Waals materials that have the potential to transform the fields of spintronics, valleytronics, opto-spin-caloritronics, and quantum computation. He has published more than 300 peer-reviewed ISI journal papers (over 14,000 citations, *h*-index: 57 from Google Scholar), 10 review papers, 8 book chapters, and 1 textbook. Presently, he serves as Managing Editor/Founding Member for the Journal of Science: Advanced Materials and Devices (IF = 7.38), the Editor for Applied Sciences (IF = 2.838), and the Editorial Board Member of Scientific Reports (IF = 4.379). He received an Honorary Doctorate Degree from Vietnam National University - Hanoi (2021), The USF Outstanding Faculty Research Achievement Awards (2017, 2019, 2021), The USF Outstanding Graduate Faculty Mentor Award (2018, HM), and The Honorary Medal by Vietnam National University - Hanoi (2018). He was also awarded a Certificate of Merit for the Development of Physical Sciences in Vietnam by the Minister of Science and Technology of Vietnam (2021). He has been featured in the list of the World's Top 2 Percent Scientists (2019, 2020, 2021). He has delivered plenary, keynote and invited talks at professional meetings on Magnetism and Magnetic Materials and organized numerous international conferences on Nanomaterials, Energy, and Nanotechnology.

Purushottam Chakraborty



Prof Purushottam Chakraborty received his PhD in Physics from the University of Calcutta and was a Senior Professor at the Surface Physics and Materials Science Division of Saha Institute of Nuclear Physics, Kolkata, India. He was an Honorary Professor of Physics at the University of Pretoria, South Africa. Soon after he had received his PhD degree, he joined the FOM-Institute for Atomic and Molecular Physics, Amsterdam and worked there for two years on "Layered Synthetic Microstructures for the realization of X-UV optical devices", in collaboration with the Philips Research Laboratories, The Netherlands. This is considered pioneering research in the field of "Optics for Soft X-rays to Extreme Ultraviolet". He indigenously constructed a Radio Frequency (RF) Quadrupole Mass Spectrometer (QMS) -based Secondary Ion Mass Spectrometry (SIMS) instrument at Saha Institute of Nuclear Physics and carried out experimental research on Ion-Matter Interactions, Inelastic Ion-Surface Collisions and Ion-Beam Analysis of Materials. His works on "Alkali-metal based Molecular-ion SIMS" have significant relevance to the exact quantification of materials in quantum-confined nanoscale systems. His other research fields include Optical Modifications of Materials, Molecular Beam Epitaxy, Low-dimensional Structures and Nanomaterials, X-UV optics, Optoelectronics, Nonlinear Optics and Photonics.

He has worked as a Visiting Professor at a number of universities and research Institutes, such as, FOM-Institute for Atomic and Molecular Physics (AMOLF), Amsterdam- Netherlands, Universite' Laval - Canada, Osaka Electro-Communication University - Japan, International Centre for Theoretical Physics (ICTP) – Italy, University of Padova - Italy, Friedrich Schiller University - Germany, Catholic University of Rio de Janeiro - Brazil, Sultan Qaboos University, Muscat – Oman, International School of Photonics, India, etc. He delivered invited lectures and plenary talks at more than 160 international conferences across the globe and authored more than 140 scientific papers including invited reviews, monographs and book-chapters. He has edited a book on *'Ion-beam analysis of surfaces and interfaces of condensed matter systems'* (Nova Science, New York) and *Journal of Physics – Conference Series* (Inst. of Physics, UK). Prof Chakraborty has been awarded the “**Most Eminent Mass Spectroscopist of India**” by the Indian Society of Mass Spectrometry and conferred ‘**Gold Medal**’ by the Chairman, Atomic Energy Commission, Government of India. He has received the prestigious ‘**Premchand Roychand Scholarship**’ and ‘**Mouat Medal**’ of Calcutta University. He is an elected Fellow of the Indian Chemical Society and West Bengal Academy of Science and Technology.

Ravinder Dahiya



Ravinder Dahiya is Professor in the Department Electrical and Computer Engineering at North-eastern University, Boston, USA. His group (Bendable Electronics and Sustainable Technologies (BEST)) conducts research in flexible printed electronics, electronic skin, and their applications in robotics, prosthetics, wearables, and interactive systems. He has authored or co-authored more than 500 publications, books and submitted/granted patents and disclosures. He has led or contributed to many international projects.

Prof. Dahiya is currently the President of IEEE Sensors Council. He has been recipient of EPSRC Fellowship, Marie Curie Fellowship and Japanese Monbusho Fellowship. He was the Founding Editor-in-Chief of IEEE Journal on Flexible Electronics and has been editorial boards of several other leading journals. He also founded the IEEE International Conference on Flexible, Printed Sensors and Systems (FLEPS) and has served as General Chair or Technical Programme Chair of

several international conferences. He has received several awards, including Technical Achievement award from IEEE Sensors Council, Young Investigator Award from Elsevier, and 12 best journal/conference paper awards as author/co-author. He is Fellow of IEEE and the Royal Society of Edinburgh.

Web: www.rsdahiya.com

Dr. Yang Yang



Yang is an internationally recognized materials scientist with primary interests in surface and interface electrochemistry of energy materials and devices, nanomanufacturing, electrochemical engineering, and nanoscience technology. He focuses on resolving the most challenging issues in energy and sustainability applications of emerging materials, for instance, aqueous batteries beyond Li-ion, direct alcohol fuel cells, water electrolysis, greenhouse gas emission reduction, and waste treatment and recycling.

A general solution to the energy and environmental crisis is to develop sustainable energy systems that can produce and store energy inexpensively and efficiently. To this end, Dr. Yang's lab is dedicated to studying the nano electrochemistry at materials interfaces, interfacial electron transportation in electrochemical systems, and light-materials interaction for solar energy harvesting.

Dr. Yang currently holds the position of Associate Professor at the NanoScience Technology Center, Department of Materials Science and Engineering, Department of Chemistry, Renewable Energy and Chemical Transformation Cluster, and the Stephen W. Hawking Center for Microgravity Research and Education, University of Central Florida.

M. S. J. Hashmi

Professor Hashmi is currently an Emeritus Professor with the School of Mechanical and Manufacturing Engineering at Dublin City University. He established this school and was its Chairman for 25 years until 2012. His research experience, interest and activities are primarily in Materials processing technologies. He earned his MSc, PhD and DSc degrees from University of Manchester and spent 19 years in research and teaching in the UK before taking up the Chair at Dublin City University where he set up the Material Processing Research Centre (MPRC) of excellence in the field of material processing. In 1990 Professor Hashmi established the International Conference Series on Advances in Materials and Processing Technologies (AMPT), a much needed international conference in materials processing. He continues to be the Chairperson of the Steering Committee for this series of conferences. In 1998 he was appointed as Editor-in-Chief of Elsevier Journal of Material Processing Technology and continued in this role until 2008.

Professor Hashmi has supervised and co-supervised 110 PhD and 55 MEng research students to successful completion. He has published in excess of 450 papers and edited 25 scientific books and

is still publishing.

In 2011, he has been appointed by Elsevier as the Editor-in-Chief of its 13 volume, 7,500 pages long Major Reference Works (in Materials Processing Technologies) published in 2014. In the same year Professor Hashmi was appointed again as the Editor-in-Chief for compiling a 3 Volume Major Reference Works by Elsevier on Manufacturing Finishing Processes.

In January 2015 he has been appointed by Elsevier as the Editor-in-Chief for a major on-line publication in Science Direct titled, Reference Module in Materials Science and Materials Engineering, which had 14 main Subject Areas and will contain about 5,000 peer reviewed articles/chapters to be compiled over 4 years. In 2019 he was appointed as the Editor-in-Chief for the 2nd Edition of the Materials Processing Technologies, MRW-MAP2E until 2024.

Currently, Prof. Hashmi is also the Editor-in-Chief for the JAMPT, published by Taylor & Francis Publishers.

Over the years, Professor Hashmi acted as External Examiner & Expert Assessor for PhD candidates and Engineering Departments with universities in Ireland, the UK, India, Pakistan, Bangladesh, Hong Kong, Canada, Australia and Malaysia.

PREFACE

Electronic materials can be considered as the physical basis of the current age of electronics, information and communication technology. These materials, integrated into numerous devices, are widely used in almost all sectors including information and communication technology, automation and control, robotics, manufacturing, process industries, instrumentation, energy and power systems, transportation, healthcare, and defence and security. Electronic materials owe their applications to certain specific properties. These properties are attributable to the flow, control, manipulation and exploitation of electrons; and their interactions with atoms, molecules and electromagnetic radiation. Electronic materials include all major classes of materials: semiconductors, dielectrics, metals, polymers, ceramics, and composites. As a field of scientific research and innovation, electronic materials have been a very active area in the past decades and is expected to grow in importance even further in the coming years.

This encyclopaedia provides advanced level students, researchers, and industry practitioners a wide and deep coverage of the foundational as well as frontier knowledge in the rapidly expanding area of electronic materials which underpin the most influential technologies of our time. The encyclopedia consists of eight sections that deal with Nanoscale Materials for Electronics; Complex Oxides; Magnetic, Spintronic, and Superconducting Materials; Photonic Materials; Organic Electronics; Sensors and Actuators; Materials for Battery and Super Capacitors; and Electroceramics- Piezoelectric, Ferroelectric and Thermoelectric Materials. There are 132 chapters in this encyclopedia. Main highlights of each section are as follows:

- The section on nanoscale electronic materials includes chapters on important materials like zinc oxide, graphene, titanium dioxide. Sol-gel synthesis of nanoscale powder production is covered as well.
- Oxides have established themselves as a very important groups of electronic materials with wide ranging applications in modern technology. The section on oxides covers topics of current interest such as strong electronic correlation in oxides, oxide surfaces and interfaces, high entropy oxides, high temperature superconductors, memristive oxides etc.
- Important topics in modern magnetisms which attract interest from both theoretical and applications points of view are included in the section on magnetic materials. This section comprises spintronics, caloritronics, multiferroics, and tunnelling magnetoresistance.
- Photonic materials are allowing innovation across diverse fields of applications. The section on photonic materials includes a rich variety of chapters. These include nonlinear optical materials, nanophotonics, nanoplasmonics, and biophotonics. Important applied topics in this section also cover photonic integrated circuits, luminescent materials, photonic sensors, and photon sources for quantum technologies.
- Electronic devices based on organic materials are getting increasingly important. The section on organic electronics contains fundamental topics, such as charge transport and mobility in organic semiconductors, single-crystal organic semiconductors, doping in organic semiconductors etc. Promising applied topics include flexible electronics, organic transistors, biocompatible devices etc.
- Sensors are going to be ubiquitous. The section on sensor and actuators comprises topics such as metal-organic framework based chemical sensors, graphene-based touch sensors, disposable pressure sensors, piezoelectric actuators, wearable strain/pressure sensors, biosensor for neurological disorders etc.
- Energy materials are the key to transitioning to our net-zero future. The section dealing with energy materials consists of chapters like MXene pseudocapacitors, advanced characterization of energy materials, metal-organic frameworks for advanced battery, solid electrolytes for lithium-metal batteries etc.
- Electroceramics continue to lead to new technologies serving wide ranging applications. The sections on electroceramics covers topics that include the following: ferroelectric devices, high-power piezoelectric materials, perovskite solar cells, thermoelectric materials, and electrocaloric ceramics.

This major reference work is available online as well as in hardcopies. Each section consists of articles written and edited by leading experts around the world. I am deeply indebted to all the Section Editors for their great efforts in selecting and editing the articles and in maintaining their quality. I highly appreciate the Elsevier team for their professional support at every stage of this work. Finally, I take this opportunity to express my sincere thanks to all authors for their contributions.

It is my hope that researchers, academics, industry professionals and students will find this encyclopedia useful.

Sincerely,
A. S. M. A. Haseeb

Introduction

Chen Jiang, Department of Electronic Engineering, Tsinghua University, Beijing, China
Arokia Nathan, Darwin College, University of Cambridge, Cambridge, United Kingdom

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In contrast to the prevailing silicon integrated circuit (IC) technology, which has formed the basis of high frequency computational devices and systems, organic electronics is relatively new and complimentary. It is suited for the lower frequency applications domain, generally in human-machine interfacing and sensing. This Volume addresses this newly emerging area with 14 chapters on organic electronic materials and devices, covering both the fundamentals and applications, highlighting differences to the inorganic counterparts and featuring their advantages in specific applications.

The fundamentals of organic electronic materials are described in three comprehensive chapters by Liu, Paterson, Xu and their co-workers. Liu provides a review on charge transport and mobility of organic semiconductors. Unlike conventional inorganic electronic materials, organic materials are bonded by the van der Waals (or weak intermolecular) force, which influences charge transport between molecules. Different mechanisms of the charge transport are discussed from a microscopic perspective, and the underlying theory and models for mobility in devices are provided from a macroscopic standpoint. Additionally, the issue of mobility measurement and extraction in the real world devices is addressed. Paterson and her co-worker provide a detailed comparison between the small-molecule and polymer semiconductors. The former family tends to form a crystalline structure, while the latter family forms high quality, uniform thin films with a disordered structure. A new approach of small-molecule/polymer blends that could offer a versatile and board range of microstructures is discussed. Insights in better forming semiconductor thin films using different kinds of blends are given, with discussions on material synthesis engineering and fabrication techniques. Xu and his co-workers present the fundamentals of doping in organic semiconductors, which is a key enabler for the formation of ohmic contacts and p-n junctions in devices. The basics of organic doping and the conventional inorganic doping of silicon are compared and contrasted, along with an introduction to different types of dopants in organic materials. Due to the different physical properties of organic semiconductors, the doping techniques should be amenable to low temperatures and low energies. Different techniques to enable organic doping are introduced, with its application to organic devices.

Techniques to process organic electronic materials are focused in the next three chapters by Hu and Ren, Yamamoto, and Korvink and co-workers. Hu and Ren provide a comprehensive review of the formation of single crystals for organic semiconductors. With the introduction to molecular aggregation modes and optoelectronic characteristics, the importance of single-crystal organic semiconductors is highlighted to realize high-performance devices. Single-crystal materials include the conventional oligoacene derivatives (e.g., pentacene and rubrene) and recently developed thiophene derivatives (e.g., BTBT and DNTT), with the latter exhibiting better resistance to oxygen and water and yielding higher mobility. Methods to grow organic single crystals are described, including physical vapor transport and solution-processed techniques, as well as their applications to field-effect transistors and phototransistors. Yamamoto presents monolayer integration of organic semiconductors. Following a brief introduction to bottom-up fabrication techniques to monolayer integration, the Langmuir–Blodgett technique, a wet process that facilitates the formation of organic amphiphilic materials at the air-solution interface, is introduced. The theory to form good packing density is presented, including methods to alter organic semiconductors to be amphiphilic along with techniques for nano-assembly. Korvink and his co-workers provide insights to nanoscale 3D printing techniques. 3D printing has provided a pathway for the rapid and inexpensive fabrication of three-dimensional components of a variety of materials, useful for a wide range of applications. The chapter provides a close look at the most promising 3D nanoprinting technologies by discussing their working principle, achievable architectural features, and demonstrated applications. They briefly discuss the current limitations, to illustrate a road map for future technological advances.

The chapters that follow address applications to electronic devices, accompanied with device physics and structural attributes. Flexible electronics at a broad glance is comprehensively reviewed by Huang and co-workers. The chemistry and structural design of flexible materials are explained, along with device structures functions of flexible electronics, with emphasis on integration and applications in electronic skin. The challenges, issues, and outlook for next-generation e-skin driven by artificial intelligence are elucidated.

Nguyen and co-workers introduce the organic materials for biocompatible piezoelectric devices, with a general overview of the fundamentals, applications, and future opportunities as well as challenges of biocompatible piezoelectric materials. To avoid any toxicity from conventional piezoelectric materials, piezoelectric biosensors and actuators are developed with advanced methods in microfabrication and materials-processing. Several naturally biodegradable piezoelectric materials that eliminate the need for invasive implant extraction are discussed. Their potential applications include sensors, actuators stimulators, ultrasound transducers, and tissue stimulators.

Xie and Xue contribute to a comprehensive survey of organic light emitting diodes. Different types of device architectures of organic light emitting diodes are discussed, along with different operation mechanisms. As one of the most successful commercial organic devices, the history of its commercialization is discussed.

Marsal and co-workers present a chapter that explains the principles and operation of organic solar cells, with the development and evolution of organic solar cells overtime. It covers the basics of organic solar cells, addressing the electronic structure of organic

semiconductor materials, and the working principles of organic solar cells, starting from the generation to the extraction of free charge. The state-of-the-art efficiency of organic solar cells is presented, as well as the upcoming research challenges for further applications.

Guo and co-workers present a thorough account of solution-processed organic thin-film transistors for displays and sensors. Device structures and process methods are introduced, with insightful discussions on suitable solutions towards systems integration for realistic applications. The key requirements of device performance for organic thin-film transistors are elaborated, with a number of exemplar applications reviewed. The future possible directions to improve organic thin-film transistors are proposed, including new semiconductor materials, device reliability solutions, and improved metal-semiconductor contacts.

Chu *et al.* provide a comprehensive review of organic electrolyte-gated transistors. Unlike the organic thin-film transistors, the electrolyte-gated transistors use an electrolyte as the dielectric, which allows the gate to modulate conduction of the semiconductor more readily. The fundamental components, mechanisms, device configurations, and figures of merit for electrolyte-gated transistors are presented, as well as different types of materials for electrolyte dielectrics. A wide range of applications are presented, including bio-sensing, wearables, electrochromic displays, electronic textiles, and neuromorphic computing.

Bonfiglio and co-workers provide a panoramic review of organic bioelectronic sensors. Four typical transistor structures and their device operation are discussed with applications to different scenarios of bioelectronic sensing. The state-of-the-art sensing applications based on organic devices are reviewed, including bioanalytical sensors, cell biosensors, and physical sensors, providing detailed operating principles and comparative advantages.

Sun and co-workers discuss organic neuromorphic systems, an emerging area bridging organic devices and the biological nervous system. Synaptic devices that mimic the function of biological synapses are introduced, detailing the mechanism and function, with both two-terminal (e.g., memristors) and three-terminal devices (e.g., transistors). The multi-input and multi-output structures that mimic the function of a neuron are presented and discussed. Their applications to intellisense, neuromorphic circuit integration and flexible e-skin are introduced, opening a new possibility to artificial intelligence systems.

All in all, the contents of this Volume demonstrate the fundamentals of organic electronic materials, fabrication techniques, and device innovations. It is hoped that this Volume serves as a useful state-of-the-art guide to organic electronics for both routine users and newcomers to the field.

Charge Transport and Mobility of Organic Semiconductors

Chuan Liu, State Key Lab of Opto-Electronic Materials & Technologies, Guangdong Province Key Lab of Display Material and Technology, School of Electronics and Information Technology, Sun Yat-Sen University, Guangdong, China

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Abstract

This chapter aims briefly discusses the carrier transport mobility in organic semiconductors. Starting from the definition of carrier mobility, we discuss the microscopic transport mechanisms and macroscopic device current-voltage characteristics. We highlight the specific features of organic semiconductors bonded by the weak van der Waals force, such as polaron, dynamic disorders, and band-to-hopping transition. By far, the measured mobility values are up to 20 cm²/Vs and enable various electronic applications, despite that some non-ideal effects exist in measurements. Further development is greatly expected based on the advances in the understanding of relationship between transport mechanisms, molecular and intermolecular structure and device technologies.

Key Points

This chapter aims at basic concepts in charge transport theories and carrier mobility in organic semiconductors:

- Definition of carrier mobility.
- Mobility and transport mechanisms: Semi-classic theory for band-like transport with trapping; Organic materials with polarons and dynamic disorders; a Highly disordered system with hopping and percolation; unified descriptions.
- Mobility and electronic devices: Metal-semiconductor-metal or a diode; organic field-effect transistors; thermal-electric bar and hall effect devices.
- Measurement and representation: Measurement methods; showing carrier mobility; Overestimating and underestimating mobility.

Introduction

Organic small molecules and polymer solids are composed of individual molecules bonded by the van der Waals force, which is a weak intermolecular force. The molecules themselves are built up by atoms with covalent bonds, which make up a relatively strong intramolecular force. Thus, the charge transport in small molecules or polymer solids is determined by the electronic structure of the individual molecules as well as the physical and energy structure of the whole solid. The latter has been regarded as the determinant role by both theoretical calculations and experiments. The same organic semiconductor could exhibit great differences in measured carrier mobility with different crystalline states or device structures. Comparative studies focusing on particular semiconductors (Kalb *et al.*, 2010a,b) have proved it and also highlight the importance of fabrication process in reducing localized states and enhancing overall carrier mobility, which is the basis to build ideal organic devices.

We will first revisit the definition of carrier mobility in organic semiconductors. Carrier mobility (μ) is taken as a figure of merit for how fast the carriers could drift in the external electric field in the microscopic view or how conductive the organic semiconductors could be in the macroscopic view. The ideal assumption of constant carrier mobility has rarely been achieved and μ is usually non-constant in device operation. Fig. 1 illustrates how the concepts of carrier mobility are differently defined and approached in general physics, crystals, and thin-film devices. In the following, we will discuss their meanings and relations. The original definition of carrier mobility (Fig. 1(a)) is the average drift velocity of a certain number of carriers in a unit electric field (Neamen, 2006):

$$\mu_{\text{drift}} = \frac{v_d}{\epsilon} \quad (1)$$

where v_d and ϵ are drift velocity and drift electric field (Fig. 1(a)). The above definition of carrier mobility has been directly used in the time of flight (TOF) (Kepler, 1960) measurement of transient current induced by electrical pulse or transient photocurrent induced by a light pulse in a conductor or diode structure:

$$\mu_{\text{TOF}} = \frac{d^2}{Vt} \quad (2)$$

where d , V , and t are transit distance, applied voltage, and time for the flight of carriers. Note that TOF experiments usually requires thick films of semiconductors.

From the original definition (Fig. 1(a)) to single crystal semiconductors (Fig. 1(b)), the original definition of carrier mobility is combined with the effective mass m^* that reflects the internal periodic potential in single crystals with accelerating time τ that reflects the scattering mechanisms, giving the microscopic carrier mobility. From single crystals (Fig. 1(b))

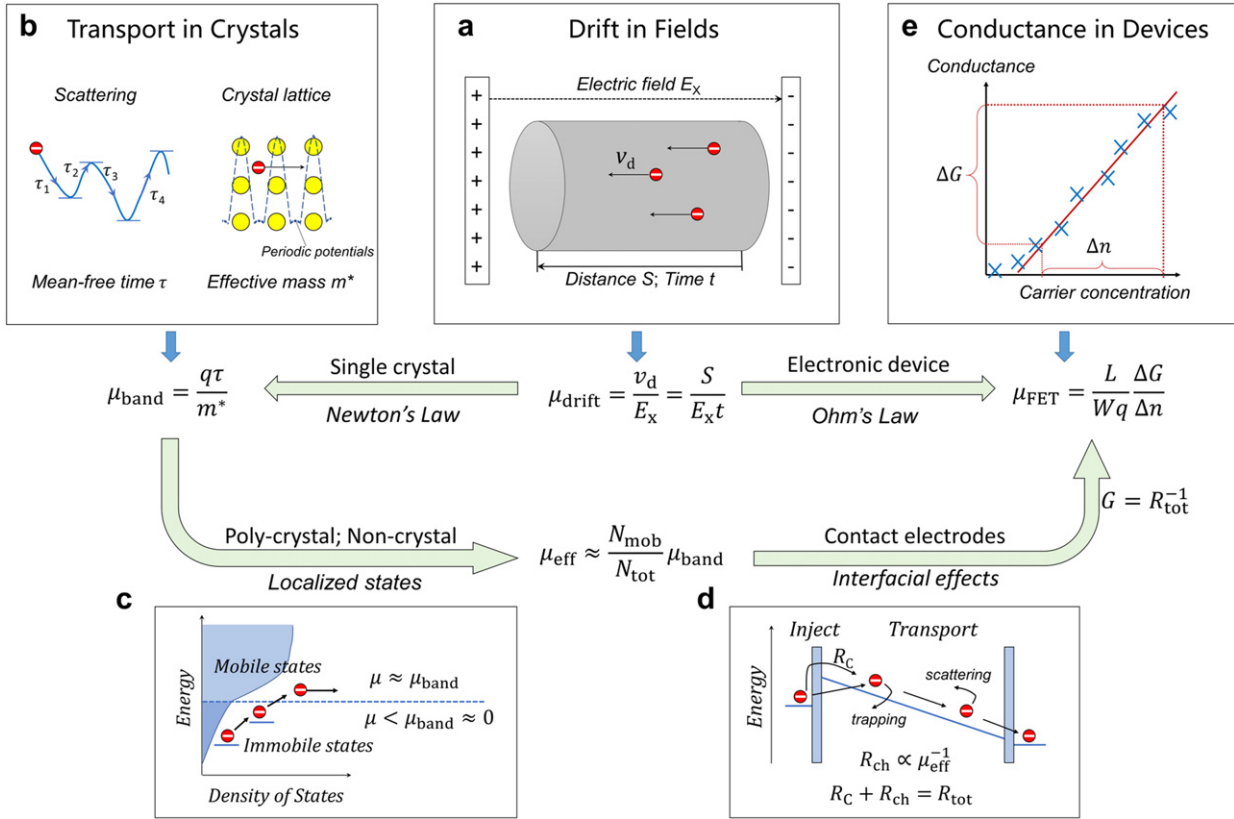


Fig. 1 The mobility family, including the mobility related to: (a) Drift in fields. (b) Transport in single crystals. The mobility equation is derived by using the Newton's law $E_x q t = m^* v_d$. (c) Transport in poly-crystals or non-crystals. (d) Transport near dielectric interfaces and between electrodes. (e) Conductance in devices. The conductance measured in FETs $G = \frac{I}{V_G}$ (for linear or non-saturated regime) is connected with the device mobility by the Ohm's law $I = W n q \mu E_x$. Adapted with permission from Tengzhou, Y., *et al.*, 2019. Understanding, optimizing, and utilizing nonideal transistors based on organic or organic hybrid semiconductors. Adv. Funct. Mater. 30, 1903889.

Table 1 Symbols for carrier mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$). The symbols put in the same row have the same meanings

Symbols	Meanings
μ_{band}	Band mobility for single crystal – Obtained by theoretical calculations (e.g. DFT).
μ_{eff} ; μ_{SC} ; μ_{tot}	Effective mobility for a semiconductor film; total mobility – Calculated by $\mu_{\text{eff}} = \frac{N_{\text{mob}}}{N_{\text{tot}}} \mu_{\text{band}}$.
μ_{lin} ; μ_{fe}	Differential mobility in the linear regime (linear mobility); field-effect mobility.
μ_{sat}	Differential mobility in the saturated regime (saturated mobility).
μ_{FET} ; μ_{dev}	Apparent device mobility from FET characterizations, including μ_{lin} and μ_{sat} .
μ_{avg}	Average mobility measuring the capability to afford current.
Average values for any μ	Average values for multiple devices (shown with errors) – e.g., $\mu_{\text{sat}} = 1.0 \pm 0.2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.
μ_{TLM}	Linear mobility extracted from TLM (transfer-line method) tests.
μ_{GFP}	Mobility measured by generalized GFP (gated four-probe) tests.
μ_{H}	Mobility measured from Hall-effect measurements.
μ_0	A parameter in Arrhenius fitting to μ -T relations – Extracted from $\mu = \mu_0 \exp\left(-\frac{E_a}{kT}\right)$. In some literature, it means <i>low-field mobility</i> , i.e. contact-corrected linear mobility.

Note: Tengzhou, Y., *et al.*, 2019. Understanding, optimizing, and utilizing nonideal transistors based on organic or organic hybrid semiconductors. Adv. Funct. Mater. 30, 1903889.

to non-crystals (Fig. 1(c)), the energy bands are disrupted in poly-crystals or non-crystals and are roughly treated with conduction levels (mobility edge) and localized states with lower energy, where the occupying carriers can hop to conduction levels with thermal, electric, or illumination energy. The carriers exhibit effective, overall mobility lower than that of the mobility in conduction levels, and the ratio between them is determined by the ratio between free carriers to localized carriers. Here, various microscopic transport mechanisms result in different forms of macroscopic carrier mobility, which will be discussed in the Section “The Microscopic View – Mobility and Transport Mechanisms”. From non-crystalline

semiconductors (Fig. 1(c)) to electronic devices (Fig. 1(d)), semiconductors are connected with electrodes and made adjacent to insulating dielectrics (if in transistors), forming the interfaces with injection barriers and interfacial trapping or scattering states. The total measured resistance comes from the injection resistance and carrier transport resistance with interfacial effects, which will be discussed in the Section “The Macroscopic View – Mobility in Electronic Devices”. From electronic devices (Fig. 1(d)) to electrical characterizations (Fig. 1(e)), total conductance is measured and carrier concentration is measured or extracted, from which the apparent device mobility is extrapolated or estimated. Here, measuring electronic devices with accurate extraction of mobility is critical to estimate the transport properties, which will be discussed in Section “Measurement of Carrier Mobility”. Different mobility is summarized first in the following Table 1.

In the following, we will take the microscopic view to revisit the carrier mobility of organic semiconductors in various charge transport mechanisms or theories. Then, we will take the macroscopic view to addressing the carrier mobility in organic electronic devices. Finally, we will discuss how to extract the carrier mobility from measurements as well as how to express it in a clear way.

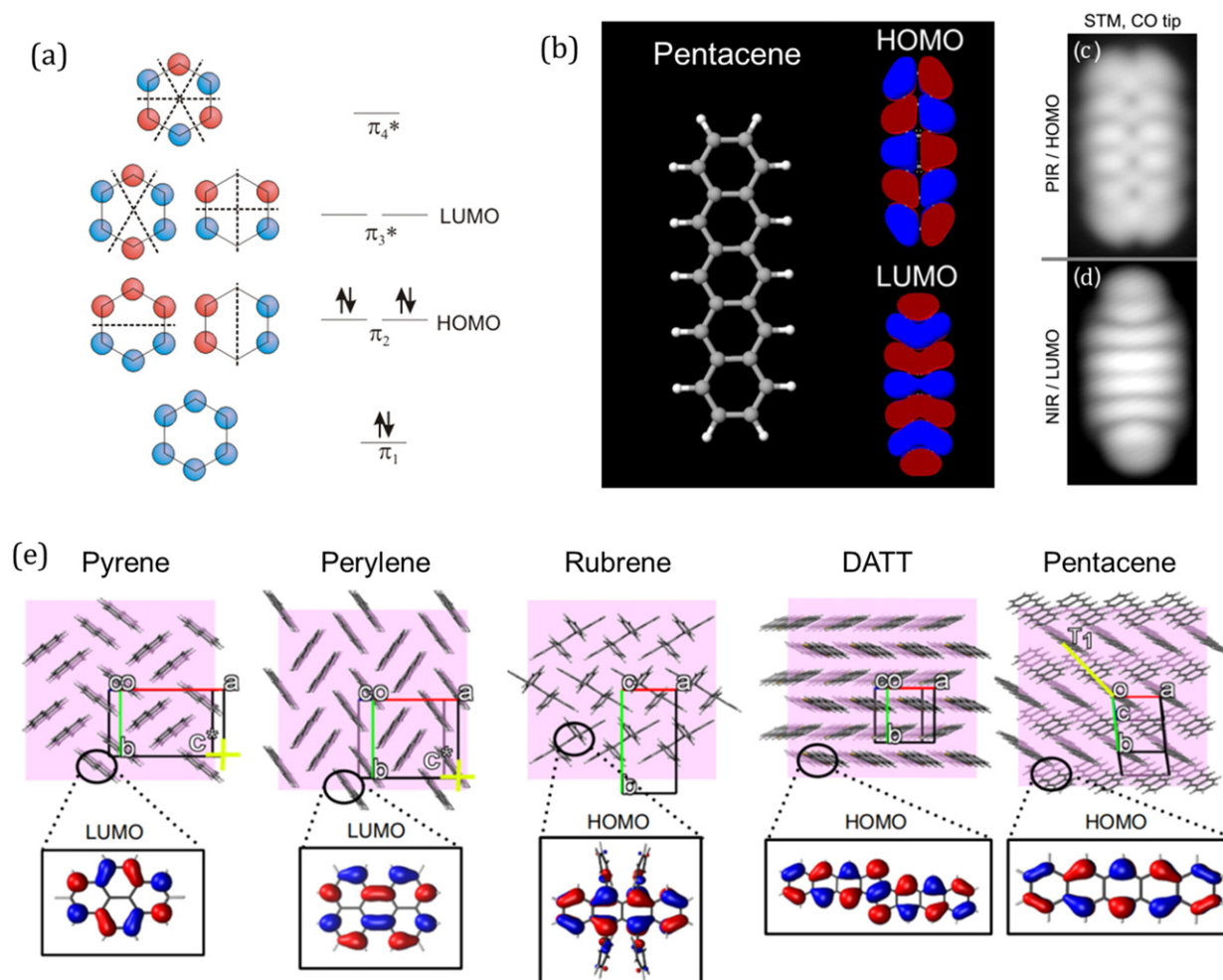


Fig. 2 The concepts of HOMO and LUMO for charge transport in organic semiconductors. (a) Molecular orbitals for the π system of Benzene (dashed lines represent nodal planes). (b) Structure model and molecular frontier orbitals HOMO and LUMO of pentacene. The colors of the atoms correspond to carbon (gray), hydrogen (white). Images were calculated with ArgusLab (ArgusLab 4.0.1, M. A. Thompson, Planaria Software LLC, Seattle, WA, <http://www.arguslab.com>). (c, d) STM measurements of pentacene on NaCl on Cu(111) using a CO tip at the onset of the positive ion resonance (PIR, a) and negative ion resonance (NIR, b). (e) Molecular herringbone layer packing for some organic semiconductors. The unit cell axes a , b , c are shown in red, green and blue, the herringbone layer is in the a - b plane, other specific directions discussed in the main text are shown in yellow. The density function theory (DFT) HOMO and LUMO of single molecules are depicted as isosurfaces where hole transfer and electron transfer is studied, respectively. Adapted with permission from Gross, L., *et al.*, 2011. High-resolution molecular orbital imaging using a p-wave STM tip. *Phys. Rev. Lett.* 107, 086101. Wertz, D.A., Molecular Science (EBook) - General Chemistry I. Vol. Chapter 6- Molecular Structure https://www.webassign.net/question_assets/wertzcams3/ch_6/manual.html. Giannini, S., *et al.*, 2019. Quantum localization and delocalization of charge carriers in organic semiconducting crystals. *Nat. Commun.* 10, 1–12.

The Microscopic View – Mobility and Transport Mechanisms

Electrons occupying the highest occupied molecular orbital (HOMO) can be excited by the lowest unoccupied molecular orbital (LUMO) to form electron-hole pairs. For a single molecule, the delocalized π system in benzene (C_6H_6) is shown in Fig. 2(a), where π electron density is spread over the entire molecule. For pentacene connecting five benzene rings together, molecular frontier orbitals HOMO and LUMO are shown in Fig. 2(b). By imaging molecular orbitals with a CO-functionalized tip at 5K, the scanning tunneling microscopy (STM) images represent the lateral gradient of the wave function (Gross *et al.*, 2011). The positive ion resonance (PIR) and negative ion resonance (NIR) reveal electrons tunnel through the HOMO or through the LUMO, respectively. The STM images acquired resemble the shape of their orbital densities as shown in Fig. 2(c and d). The HOMO and LUMO of more complicated and commonly researched small molecular semiconductors are shown in Fig. 2(e), together with their herringbone layer packing structures. In organic solids, HOMO and LUMO of individual molecules overlap with each other and form dense energy levels with very small energy differences, forming a quasi-continuous energy band.

However, the concept of energy band in Van der Waal bonded organic semiconductors is not as strict as that in covalently bonded inorganic semiconductors. From the point of view of materials structure, most organic semiconductor films lack long-range periodic order because of the structural disorder caused by the micro-domain boundaries, twisting of polymers, or chemical residues. The relatively low carrier mobility ($< 30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), together with the generally occurred strong electron-phonon coupling, which produces a mean free path approximately equal to the lattice constant, make assumptions of coherent band transport self-consistent only in highly ordered organic crystals. Delocalized carriers with band-like, coherent transport can be disturbed by lattice vibration, whereas localized carriers with hopping, incoherent transport can be assisted by thermally-activated vibration (Fig. 3(a)). The difference between band models (or delocalized, coherent transport) and polaron transport models (or hopping, incoherent transport) could also be illustrated by the extending area of carrier probability function as shown in Fig. 3(b). Generally, from low disorder to high disorder, carrier mobility could be mainly understood within the band transport or hopping models, roughly depending on the mobility values (Fig. 3(c)).

In more detail, different theories concerning microscopic charge transport mechanisms have been proposed and many of them have been supported by evidence in different experiments on the temperature dependence of carrier mobility with various materials (Troisi, 2011; Coropceanu *et al.*, 2007; Horowitz, 2004). A brief summary of charge transport theories is given in Fig. 4, in which the theories are roughly classified according to the crystallinity or structural disorder of the semiconductors. The following are several theories developed to model the charge transport in organic semiconductors and to derive microscopic mobility as a function of various parameters.

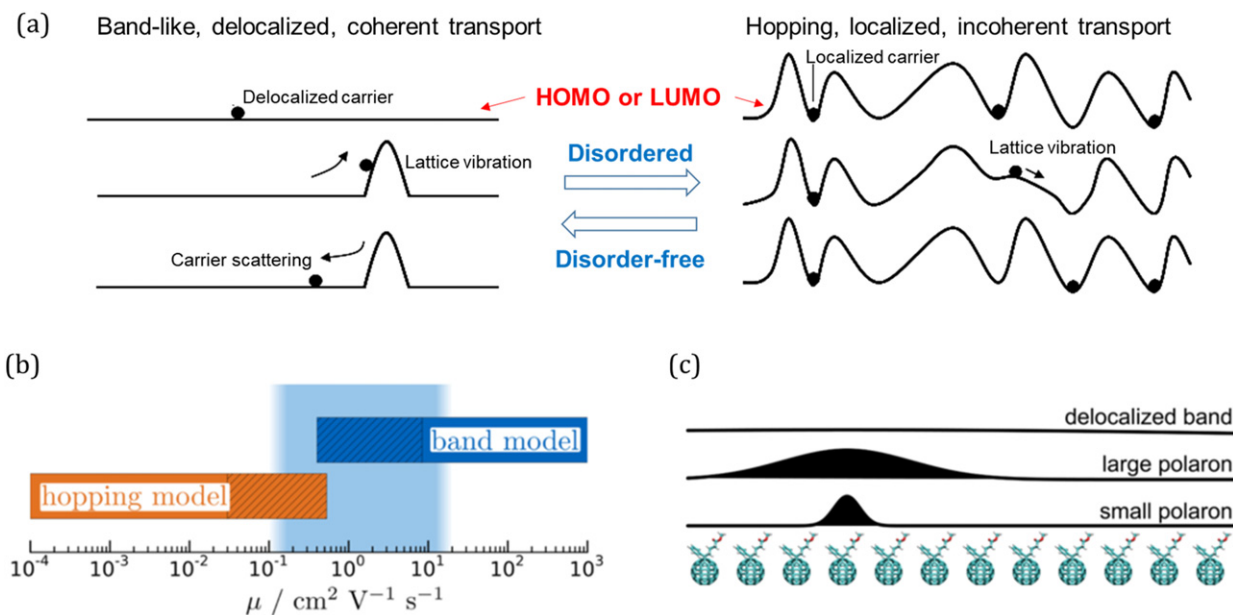


Fig. 3 Band-like transport and hopping transport in HOMO or LUMO levels. (a) Illustration of band transport (left), where a delocalized carrier moves as a plane wave and is scattered by lattice vibrations or phonons that disrupt the crystal symmetry; and hopping transport, where a localized carrier moves assisted by thermal activated lattice vibration. (b) Illustration of charge carrier localization in a molecular crystal: (top) Carrier probability function in a fully delocalized band; (middle) large polaron delocalized over a number of molecular sites; (bottom) small polaron localized near a single site. (c) Charge transport regimes and theories for organic semiconductors. Adapted or modified with permission from Pope, M., 1999. C. E. S. Electronic Processes in Organic Crystals and Polymers, second ed. Oxford University Press. pp. 337–340. Oberhofer, H., *et al.*, 2017. Charge transport in molecular materials: An assessment of computational methods. Chem. Rev. 117, 10319–10357. Giannini, S., *et al.*, 2022. Charge transport in organic semiconductors: The perspective from nonadiabatic molecular dynamics. Acc. Chem. Res. 55, 819–830.

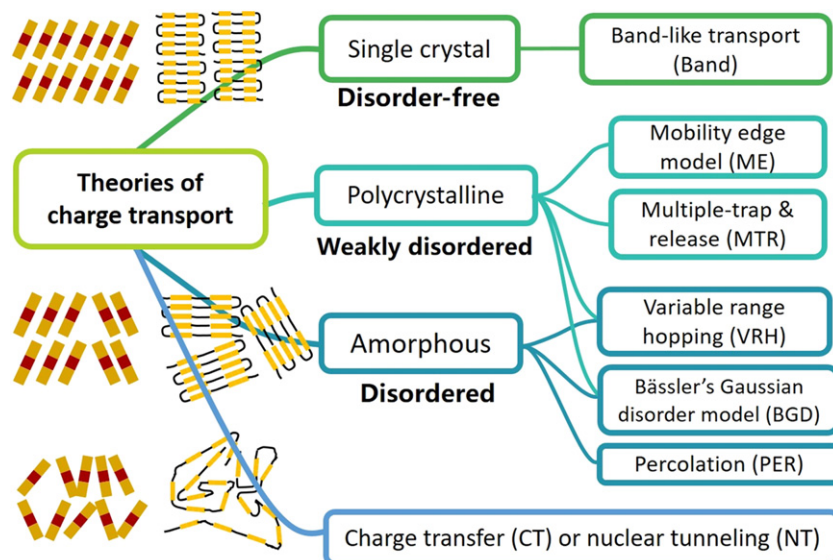


Fig. 4 A brief summary of charge transport theories in organic semiconductors. According to the degree of order or crystal structure of the semiconductor, these theories can be roughly divided into several categories. Adapted with permission from Liu, C., *et al.*, 2017a. A unified understanding of charge transport in organic semiconductors: The importance of attenuated delocalization for the carriers. *Mater. Horiz.* 4, 608-618.

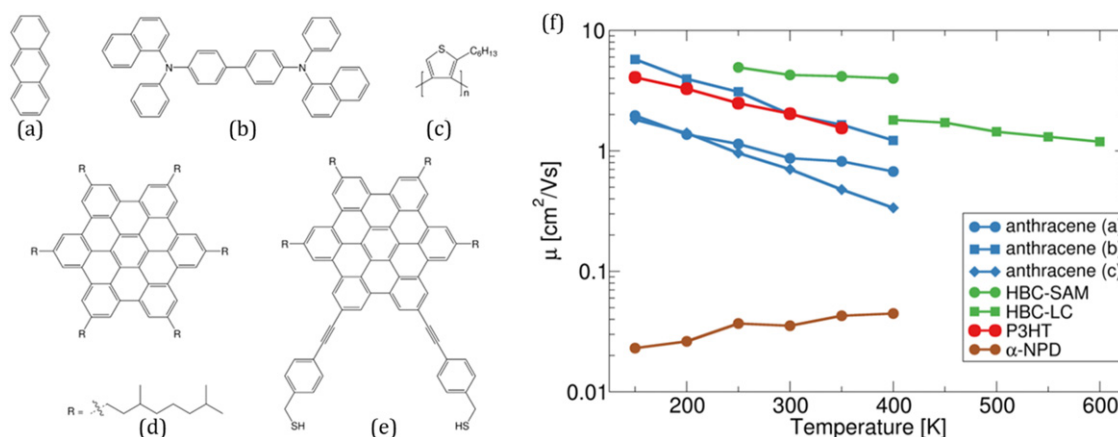


Fig. 5 Band-like transport mobility in organic semiconductors. (a) Temperature-dependent mobilities of some organic semiconductor single crystals (simulated by theory). (b-f) Molecular building blocks of: (b) anthracene, (c) N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (α -NPD, disordered materials), (d) regioregular poly(3-hexylthiophene) (P3HT), (e) a hexabenzocoronene (HBC) derivative with racemic branched (3,7-dimethyloctanyl) side chains (HBC-LC), and (f) HBC-based self-assemble monolayer (HBC-SAM). Adapted with permission from Heck, A., *et al.*, 2016. Simulation of temperature-dependent charge transport in organic semiconductors with various degrees of disorder. *J. Chem. Theor. Comput.* 12, 3087-3096.

Semi-Classic Theory for Band-Like Transport With Trapping

Band-like transport. The mobility of single crystalline organic semiconductors is regarded as the upper limit of a certain material. Classic band-like transport is appropriate for disorder-free organic semiconductors, which are mainly single crystalline (Hulea *et al.*, 2006; Ding *et al.*, 2010; Ciuchi *et al.*, 2012a; Ji *et al.*, 2019) or some conjugated polymers with extremely low torsions of chains (Venkateshvaran *et al.*, 2014). In single crystals with perfect lattice and periodic potentials (Fig. 3(a, c)), electrons or holes are accelerated by the external electric field between each collision, and the average time between successive collisions is defined as the mean free time. The accelerated velocity between each collision is then determined by the electric field E_x , using Newton's law in the form of momentum, i.e., $v_d = -\frac{qE_x\tau}{m^*}$. The effective mass m^* characterizes the structure of the maximum or minimum of the valance or conduction band formed in the periodic potentials of the lattices, i.e., $m^* = \frac{1}{\hbar} \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1}$ (E is the energy of electrons and k is the wave vector). The mean-free time of the carriers τ is reversely proportional to the frequency of collision between carriers and the lattice. Then, according to the definition, the mobility of single crystal is defined as:

$$\mu_{\text{band}} = \frac{v_d}{E_x} = \frac{q\tau}{m^*} \quad (3)$$

where the subtitle *band* rises as the effective mass m^* characterizes the energy band, and the mean free time could be estimated as $\tau = \frac{\lambda}{v} \approx \frac{\lambda}{\sqrt{2k_B T/m^*}}$ and λ is the mean-free path. The mean free time τ is affected by various scattering mechanisms, including phonons, defects, impurities, etc.:

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{phonon}}} + \frac{1}{\tau_{\text{defect}}} + \frac{1}{\tau_{\text{impurity}}} + \dots \quad (4)$$

Apparently, the smallest time constant mainly affects the mobility characteristics. The band-like transport limited by phonon scattering in single crystalline organic semiconductors is usually manifested in mobility that decreases if temperature increases, in the form of $\mu \propto T^{-\alpha}$, where α is constant close to 1 (Fig. 5).

The values of m^* and μ_{band} could be predicted by DFT calculations on intermolecular electronic coupling, molecular reorganization energy, molecular packing structure, and band structure with considering the electron-phonon scatterings, including all intra- and inter-molecular vibrations (Hua *et al.*, 2012; Zhigang *et al.*, 2015). In the case that intermolecular interaction is weak with small delocalization degree, the energy band is very narrow (a few $k_B T$) with large effective mass m^* : (Pope, 1999)

$$\mu_{\text{band}} = \frac{q\tau}{k_B T} \left(\frac{J^2 a^2}{\hbar^2} \right) \quad (5)$$

Where J represents the intermolecular interaction energy, a is the nearest-neighbor lattice constant, τ is the average relaxation time, k_B is the Boltzmann's constant, T is the temperature, and q is the electron charge. In the case that intermolecular interaction is relatively strong with large delocalization degree, the energy band is relatively wide with small effective mass m^* . The large transfer integrals indicate a large theoretical carrier mobility.

With the band model, the distribution of carriers describing the density of carriers in state k at position r can be considered in the Boltzmann formalism. The carrier mobility based on statistics of velocity and relaxation time of the k state is given as:

$$\mu_{\text{band}} = \frac{q}{m^*} \frac{\tau v^2}{v^2} \approx \frac{q}{k_B T} \tau(k) v(k) v(k) \quad (6)$$

Different inspections or assumptions of statistics for velocity and relaxation time could be substituted into the above equation to give the total average band mobility (Pope, 1999).

The band-like transport is usually discussed together with multiple trap and release model if organic semiconductors are polycrystalline, while pure hopping transport is mainly considered if organic semiconductors are highly disordered (e.g., amorphous polymers) (Salleo, 2007; Haneef *et al.*, 2020), as shown in Fig. 6(a). For polycrystalline organic semiconductors with a low extent of structural disorder, the mobility edge (ME) model is applicable and it is similar to the multiple trap and release (MTR) model (Coropceanu *et al.*, 2007; Brotherton, 2013a; Seto, 1975; Levinson *et al.*, 1982; Voutsas, 2003; Horowitz, 1998a; Le Comber *et al.*, 1970). The ME and MTR assume that the charge carriers are delocalized and mobile above the well-defined transport energy level, i.e. the mobility edge or band edge, and trapped at the highly concentrated localized state and immobile below it. This is schematically shown in Fig. 6(b). Transport only occurs when carriers are thermally activated to the mobile states, move under an applied electric field, and then become trapped again as soon as they arrive at a trap state. This model does not make an assumption as to what the nature of the transport level may be. This model was first examined in detail by Mott (1967) for silicon and later developed by Le Comber and Spear for hydrogenated amorphous silicon (α -Si: H) (Le Comber *et al.*, 1970). In general, if carriers are trapped and released repeatedly, the effective microscope mobility is related to the intrinsic band-mobility by the ratio (Bube, 1978):

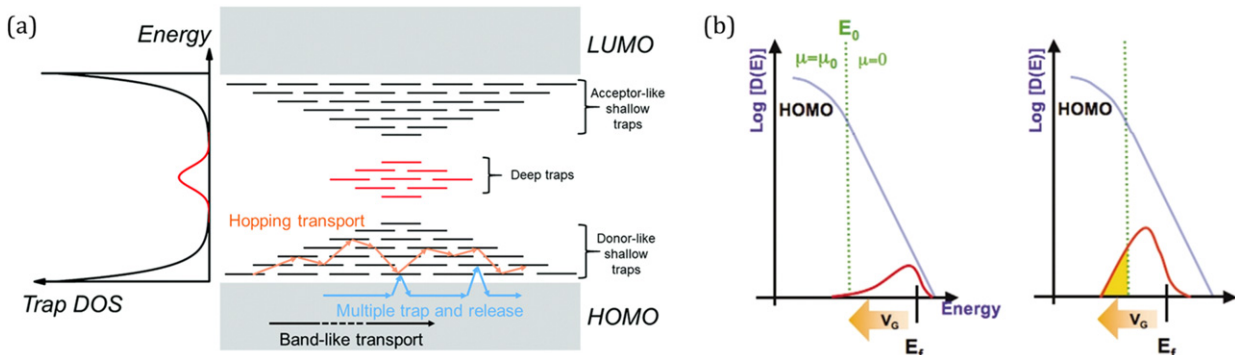


Fig. 6 Energy levels and mobility edge model. (a) A scheme of band-like transport, multiple trap and release (MTR), and hopping transport, together with acceptor-like states and donor-like states near the conduction band (CB) or LUMO edge. (b) A scheme of thermally activated transport with a mobility edge. (b) is adapted with permission from Salleo, A., 2007. Charge transport in polymeric transistors. *Mater. Today* 10, 38–45.

$$\mu_{\text{eff}} = \mu_0 \frac{\tau_0}{\tau_0 + \tau_T} \quad (7)$$

where τ_0 is the mean-free time for drift in acceleration and τ_T is the mean trapping time in traps. In general, no assumption is made about the transport mechanism above the transport level, and also the only assumption made regarding the trap levels is that they have a mean trap energy E_T (or activation energy E_a) below the transport level. The temperature dependence of the mobility is, therefore, Arrhenius-like and is given by:

$$\mu = \mu_0 \frac{N_C}{N_t} \exp\left(-\frac{E_T}{k_B T}\right) \quad (8)$$

where μ_0 is the mobility above the transport level (usually regarded as that in Eq. 12) and N_C/N_t is the ratio of the effective density of states at the transport level to the concentration of traps, and E_t is the mean energy of the trap states (Horowitz, 1998b). The distribution of charges, and hence the mobility, are determined by the distribution of traps, temperature, and the voltage applied. Due to the simple form, the ME or MTR model has been one of the mostly used to reasonably capture the transport characteristics and activation energy of high-mobility organic FETs (Chang *et al.*, 2006; Salleo *et al.*, 2004). The Arrhenius-like mobility has been

The assumptions of a well-defined mobility edge and a constant mobility above the transport level may be oversimplified for disordered organic materials, and it would be preferable for mobility to vary as a function of energy. Also, in organic semiconductors, the assumption that charge transport does not affect the well-defined transport level may not be always valid, as transport may induce local deformation of the molecular packing structure as described below. The above discussion about band-like transport borrows the classic semiconductor theory developed for covalently bonded, inorganic crystals. In fact, the understanding of transport in organic single crystals with van der Waals force has been developed well beyond the semi-classical band-theory frameworks and gained more experimental support.

Polaron Hopping and Dynamic Disorders

In organic semiconductors, carrier transport would affect the local polarization environment, as the low- k feature and weak intermolecular interaction. Charge transport along the polymeric backbone or molecular packing would require reorganization energy and the polarization effect exists, where charges induce local deformation of the lattice. Thus, the small polaron transport or Marcus charge transfer (CT) model (Yin *et al.*, 2011; Marcus, 1956, 1993; Yavuz *et al.*, 2015a; Lu *et al.*, 2018) should be considered. The CT theory defaults to a hypothesis that the charge transport in organic materials is in the form of a “small” polaron, where the dimensions of the deformation are of the order of an intermolecular spacing (Horowitz *et al.*, 1999; Beljonne *et al.*, 2001). The CT theory, also referred to as electron transfer (ET), is a thermodynamic process by which an electron or a charge moves from one molecule to another or, in chemical terms, a redox process among donor and acceptor moieties occurs. It is proposed by Marcus at first who presumed that electron transfer occurs between two unconnected chemicals which remain separate species, widely observed in biochemistry systems (Marcus, 1957, 1960). The theory was then extended by Hush, in which electron transfer occurs via a

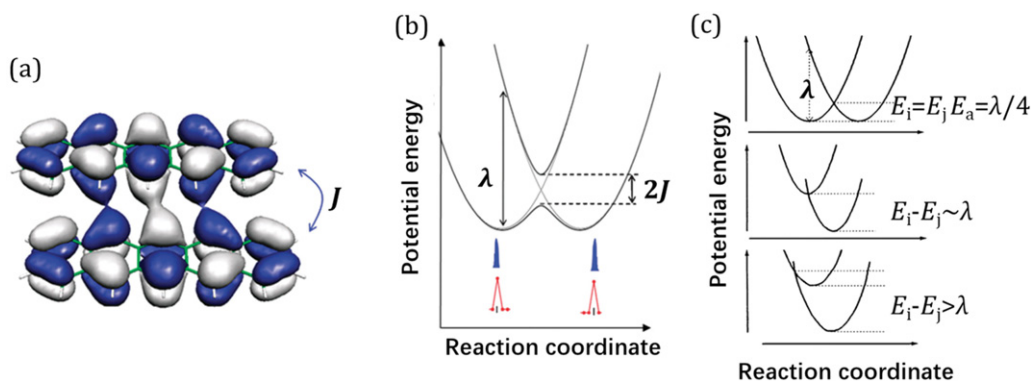


Fig. 7 Charge transfer mechanisms. (a) The electronic coupling or transfer integral J is approximately proportional to the overlap between molecular orbitals of two neighboring molecules (the HOMO orbitals of two neighboring pentacene molecules are represented). (b) Transfer integral J , reorganization energy λ , and static or dynamic disorder. (c) Potential energy curve for the process of *adiabatic* hopping to the neighboring site. (d) Potential energy curve for the process of *non-adiabatic* hopping to the neighboring site, for different cases of ground state energies. (e) Localization of excess charge in an electron donor – acceptor (D-A) system. Non-adiabatic and adiabatic energy curves for electron transfer are drawn in dashed (black) and solid lines (red), respectively. From left to right, electronic coupling between molecules gets stronger and the excess charge carrier changes from localized to delocalized. (a) Adapted with permission from Troisi, A., *et al.*, 2005. Band structure of the four pentacene polymorphs and effect on the hole mobility at low temperature. *J. Phys. Chem. B* 109, 1849–1856. (b) Sosorev, A.Y., 2020. Simple charge transport model for efficient search of high-mobility organic semiconductor crystals. *Mater. Des.* 192, 108730. Gajdos, F., *et al.*, 2013. On the inapplicability of electron-hopping models for the organic semiconductor phenyl-C61-butyric acid methyl ester (PCBM). *J. Phys. Chem. Lett.* 4, 1012–1017 (c) Modified with permission from Oberhofer, H., *et al.*, 2017. Charge transport in molecular materials: An assessment of computational methods. *Chem. Rev.* 117, 10319–10357.

covalent linkage between the donor and acceptor (Hush, 1967, 1985). This is otherwise called an inner sphere ET, and is usually used to describe the ET in transitional metal complexes (Creutz *et al.*, 1969) and mixed-valence organic systems (Coropceanu *et al.*, 2002).

The most important points of the CT theory are: (1) When an electron is excited from a donor to an acceptor or hops from one site to the other, the required energy “reorganization energy” (λ in Fig. 7(b)), is intimately related to the activation energy for thermal electron transfer process. (2) The rate of CT from one site to another will increase with the thermodynamic driving force for the reaction to a critical value, and decrease again when the driving force further increases. The electronic transfer integral J (Fig. 7(a)) is large in adiabatic reaction, and the coupling between the neighboring molecules states is strong. The crossing to higher order states in the reaction coordinate is avoided with an energy gap of $2J$ and CT may follow the pathway of the lower potential curve in Fig. 7(c). The hopping rate for the adiabatic process could be described by:

$$k_{CT,A} = \frac{\omega}{2\pi} \exp\left(-\frac{\lambda/4 - J}{k_B T}\right) \quad (9)$$

where ω is frequency of molecule, J denotes the charge transfer integral and λ is the total reorganization energy. Generally, band-like transport dominates if J is large (strong coupling) but λ is small (weak polarization), while hopping transport dominates with a small J and a large λ .

In contrast, in non-adiabatic reactions or intramolecular long-distance electron transfer (Closs *et al.*, 1988) (Fig. 7(d)), there is not enough time for the wave function to evolve in the crossing region of the reaction coordinate and charges are reflected back many times before it finally jumps to the upper acceptor surface. The non-adiabatic charge hopping between two molecules can move via thermal activation and the activation energy is $\lambda/4$. Alternatively, the electron can move by optical excitation from one minimum of the lower adiabatic surface to the Frank-Condon state of the upper adiabatic surface (vertical transition without changing the coordinate). This process requires the reorganization energy of λ . By applying an electric field, the activation energy can be reduced and vanish in the case of $E_{ij} = E_i - E_j = \lambda$ (Fig. 7(d), top). If the electric field further increases, the activation energy will reappear and thus, the electron transfer rate will be expected to decrease again (Fig. 7(d), middle and bottom). Charges move by thermally activated transfer between adjacent sites or molecules with a rate k_{CT} of (Troisi, 2011; Jortner, 1976):

$$k_{CT,NA} = \frac{4\pi^2 J^2}{h} \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{(E_{ij} - \lambda)^2}{4\lambda k_B T}\right] \quad (10)$$

where J denotes the transfer integral, E_{ij} is the free energy gained or lost by the charge upon transfer (also refereed as the difference in site energies), and λ is the total reorganization energy. The site energy difference E_{ij} is minimized in highly crystalline structures and large with distribution in morphology with a high degree of disorders. In electron transfer between donor and acceptor, when electronic coupling is weak (small J), excess electrons are fully localized on the donor ($J \ll \lambda$, Fig. 7(e) left) or a small fraction of them are delocalized over the electron acceptor (Fig. 7(e) middle); when electronic coupling is strong (J is close to λ , Fig. 7(e) right), the excess electron is delocalized over donor and acceptor (Gajdos *et al.*, 2013). Therefore, high delocalization with a high

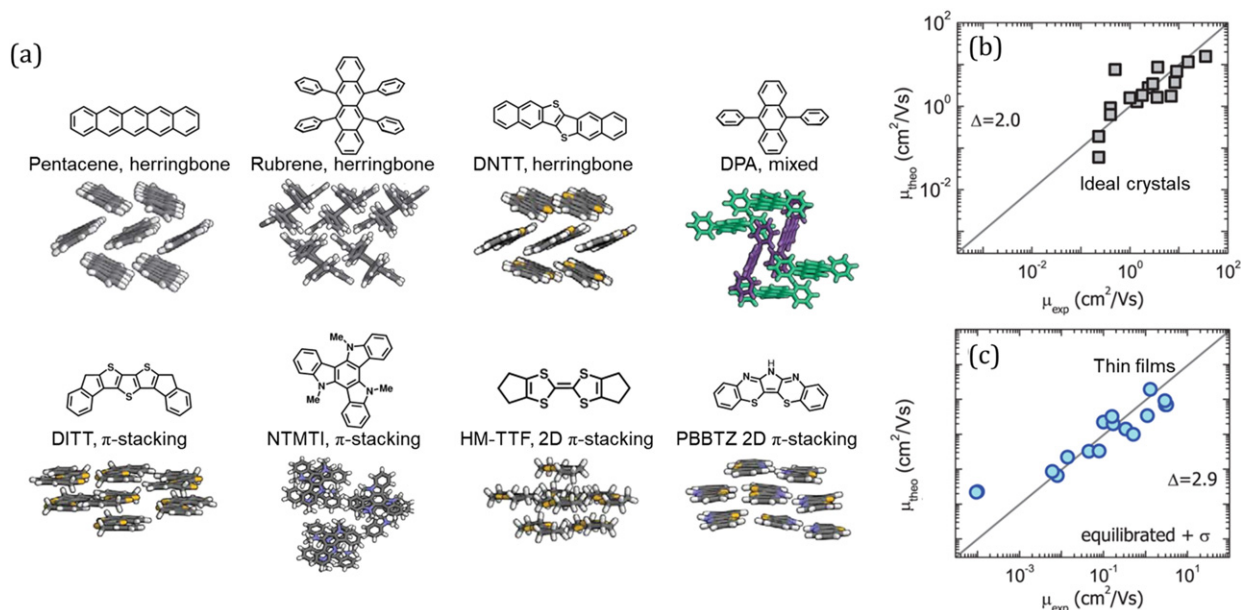


Fig. 8 Carrier mobility calculated based on Marcus rates and the kinetic Monte Carlo method. (a) Inter-molecular packing morphologies obtained by molecular dynamic simulations equilibrated at 300K. (b, c) Correlation between experimentally measured hole mobility and their calculated values for (b) ideal crystals or (c) thin films with equilibrated morphology and site energies. Adapted with permission from Yavuz, I., *et al.*, 2015b. Theoretical study of the molecular ordering, paracrystallinity, and charge mobilities of oligomers in different crystalline phases. J. Am. Chem. Soc. 137, 2856–2866.

charge-transfer rate and a high mobility requires large transfer integrals J symbolizing strong electronic coupling and a full compensation between E_{ij} and λ . The quantitative electron–phonon interaction in charge transport can be quantum-mechanically described based on ab initio material parameters (Ortmann *et al.*, 2011). Polaronic transport has been demonstrated to be an important mechanism in disordered organic solids, particularly molecularly doped polymers (Schein *et al.*, 1990; Schein, 1992).

The hopping rate k_{CT} could be used in simulations to calculate the carrier mobility by Einstein formula $\mu = qD/k_B T$. The diffusion coefficient D is obtained based on the CT rates k_{CT} in Eq. (10) combined with specific crystal structures and energetic disorder arising from variations in site energies, achieved by kinetic Monte Carlo simulations and averaging over a large amount of trajectories (Jiang *et al.*, 2019). Site energy is the change in energy of the complex when the charge of a molecule changes. The site energy difference E_{ij} in Eq. (10) is the change in site energies of molecular pairs i and j participating in the charge-transfer reaction. Examples of calculating mobilities of certain molecules with certain packing structure are shown in Fig. 8, (Yavuz *et al.*, 2015b) where molecular dynamics (MD) simulations are employed to equilibrate crystal morphologies at 300K. The simulation results coincide with small errors (Δ) with the experimental results in single crystals and thin films. For thin films, the simulations include the thermal disorder as the ensemble distributions in centroid distances between neighboring molecules and energetic disorder σ as the standard deviation in Gaussian-distribution site energy differences. In general, the calculated mobility roughly follows the Arrhenius-like temperature-dependent mobility.

Furthermore, as the CT is driven by the coupling to nuclear vibrations (i.e., *heat bath*), (Asadi *et al.*, 2013) the effect of the local nuclear configurations should be taken into account, especially for non-polar Organic semiconductors where the relevant stretching vibrations are at high frequency. This mechanism is described by the quantum nuclear tunneling (NT) theory (Asadi *et al.*, 2013; van der Kaap *et al.*, 2016; Nan *et al.*, 2009; Jiang *et al.*, 2015), in which the carriers tunnel through the potential formed by the coupling of the electronic charge to its nuclear environment. Compared to the CT theory, the NT theory predicts higher values of mobility in Organic semiconductors that are consistent with some experimental results (Jiang *et al.*, 2016; Geng *et al.*, 2012). Note that CT and NT theories are generally considered in single crystalline organic semiconductors to estimate the intrinsic band mobility and in poly-crystalline organic semiconductors to understand the energy-dependent charge transport (Chang *et al.*, 2006; Lu *et al.*, 2018). Anisotropy of carrier mobility can be calculated by including the NT theory as shown by Shuai *et al.* in Fig. 9, (Jiang *et al.*, 2019) where pentacene, rubrene, dinaphtho-thieno-thiophene (DNTT), and dianthra-thieno-thiophene (DATT) are typical *p*-type materials and *N,N'*-bis(*n*-C₃F₇CH₂)-(1,7 and 1,6)- dicyanoperylene-3,4: 9,10- bis(dicarboximide)s (PDIF-CN2) is *n*-type materials. Rubrene possesses the strongest anisotropic transport property, while DNTT has the weakest anisotropy, in good agreement with experimental results (Sundar *et al.*, 2004; Xie *et al.*, 2013).

Despite the small polaron considerations above have been used, there has also been argument in terms of practical applicability of small polarons in organic semiconductors (Troisi, 2011; Troisi *et al.*, 2006a). Besides the longstanding consensus on large transfer integrals with strong electronic coupling, thermal molecular motions cause large fluctuations in the intermolecular transfer integrals which localize the charge carrier. That is, in the quantum Hamiltonian for the electron, the off-diagonal elements are modulated as the nuclear positions are fluctuated (Troisi *et al.*, 2006b). This effect destroys the translational symmetry of the electronic Hamiltonian and makes the band description inadequate for organic crystals. *Dynamic disorder* arises from

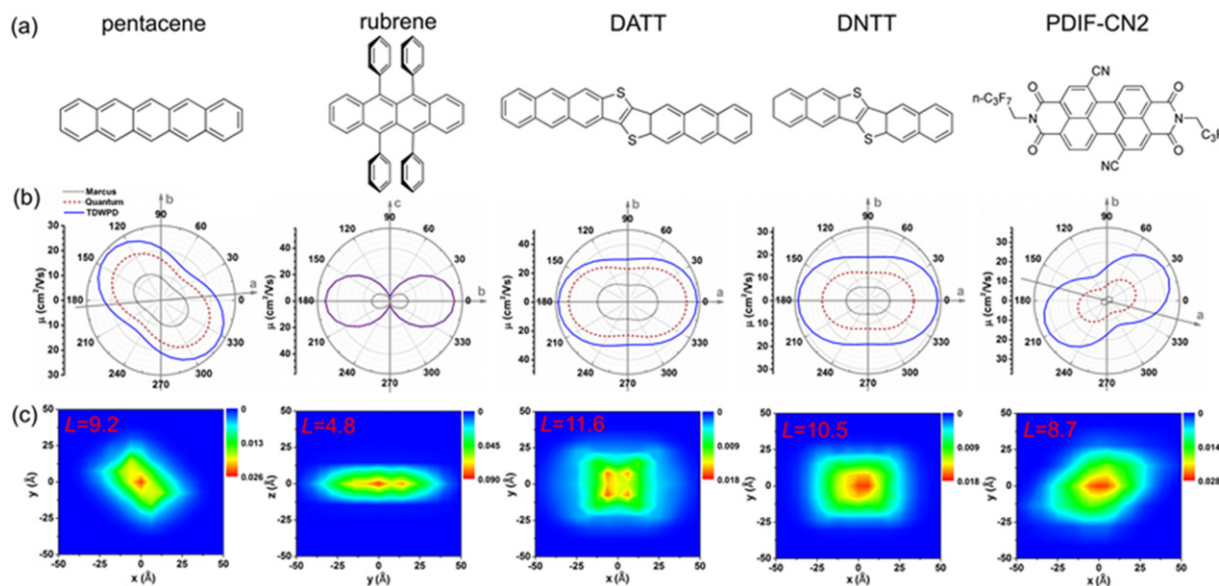


Fig. 9 Isotropic mobility in organic semiconductors. (a) Molecular structures. (b) The anisotropic mobilities resulting from Marcus, quantum nuclear tunneling, and time-dependent wave packet diffusion methods (including the quantum nuclear effect by the harmonic oscillator model). (c) The distributions of charge population and the 2D electronic delocalization lengths (“ L ”). (a) Figure adapted with permission from Royal Society of Chemistry. (b) Adapted with permission from Jiang, Y., *et al.*, 2019. Understanding carrier transport in organic semiconductors: Computation of charge mobility considering quantum nuclear tunneling and delocalization effects. *J. Chem. Theor. Comput.* 15, 1477–1491.

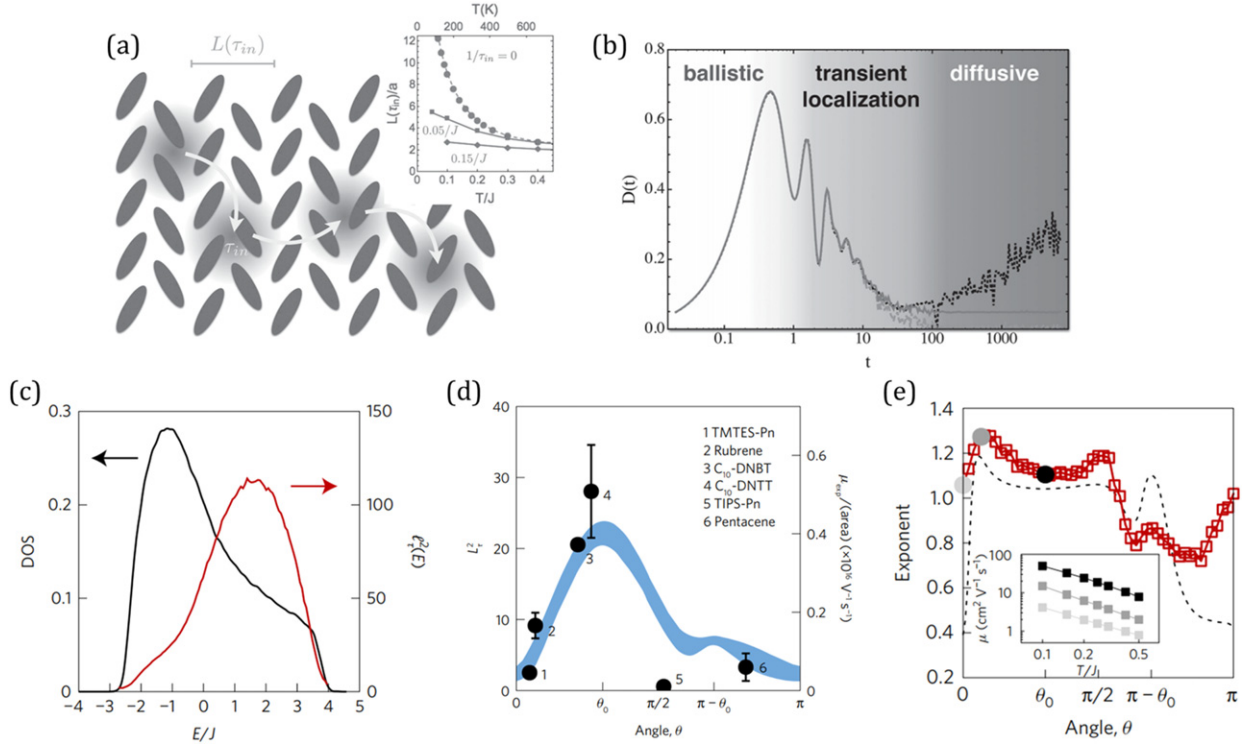


Fig. 10 Dynamic disorder with transient localization or delocalization. (a) Instantaneous diffusivity $D(t) = d\Delta X^2(t)/dt$ extracted from the experimental optical conductivity (inset). The continuous line is the extracted value and the dashed-dotted line is the theoretical calculations with the relaxation-time approximation. (b) Calculated squared transient localization length L_t^2 as a function of the azimuthal angle $\theta = \cos^{-1}(J_a/J)$, where $J^2 = J_a^2 + J_b^2 + J_c^2$ and J_a , J_b and J_c represent the average values of nearest-neighbor transfer integrals in three directions. Inset represents the distribution of data marked with circles in the main panel. (c, d) Transient localization and anisotropic mobility: (c) saturation transistor mobility anisotropy measured in a single crystal tetracene field-effect transistor with the dashed line as an empirical fit; the micrograph of a tetracene crystal transistor (scale bar shows 100 μm) is shown on the right. (d) mobility and phonon directions in a single crystal tetracene with Mode II and Mode III motions related to of transient localization that changes mobility. (a) Modified with permission from Ciuchi, S., *et al.*, 2011. Transient localization in crystalline organic semiconductors. *Phys. Rev. B* 83, 081202. (b) Adapted with permission from Nematiraram, T., *et al.*, 2019. Practical computation of the charge mobility in molecular semiconductors using transient localization theory. *J. Phys. Chem. C* 123, 6989–6997. Bittle, e.g., *et al.*, 2019. Correlating anisotropic mobility and intermolecular phonons in organic semiconductors to investigate transient localization. *Commun. Phys.* 2, 1–7.

intermolecular vibrations or fluctuations, (Alessandro, 2011; Fratini *et al.*, 2016) and causes a transient localization over a length L_t within a fluctuation time τ_{in} , which is given by the inverse of the typical intermolecular oscillation frequency. Charges are transiently localized within the time proportional the timescale of molecular motions, $\tau_{in}\bar{\Gamma}/\omega_0$, before restoring the diffusion (Fig. 10(a), indicated by the blue arrow). The corresponding instantaneous diffusivity $D(t) = d\Delta X^2(t)/dt$ is shown in Fig. 10(a). The $D(t)$ increases at short times in the ballistic regime, decreases with oscillation in the transient localization regime (signaling the backscattering due to Anderson localization), and then increases or reaches a constant in the diffusive regime. Based on $D(t)$, the mobility in crystal becomes (Fratini *et al.*, 2016).

$$\mu = \frac{qL_t^2}{2k_B T \tau_{in}} \quad (11)$$

The L_t is the critical transient localization length provided by quantum localization corrections (Ciuchi *et al.*, 2012b), i.e. $L_t^2 = \tau_{in}^{-1} \int \Delta X^2(t) \exp(-t/\tau_{in}) dt$, where $\Delta X^2(t)$ is the spread or squared displacement. Different from band and hopping theories which ask for absolute large transfer integrals, the mobility in the transient localization regime is sensitive to the relative transfer integrals in the different bond directions. The theory highlights the importance to minimize the dependence of the intermolecular transfer with intermolecular distance and increasing the intermolecular vibration frequency ω_0 by tightening the intermolecular bonds. A map of L_t of high-mobility molecular semiconductors has been developed to identify what patterns of nearest-neighbor transfer integrals reduce the effect of dynamic disorder (Fratini *et al.*, 2017). The prediction coincides with the experimental results of FET with small molecular crystals. An example of energy-resolved transient localization length is shown in Fig. 10(b). As the carriers tend to be more and more localized upon increasing the thermal molecular disorder, the localization length L_t decreases with temperature T ($\mu \sim T^{-p}$). The prediction of a series of L_t values coincides with the experimental results of FET with small molecular crystals (Fratini *et al.*, 2016, 2017).

The concept of dynamic disorder has been supported by diffuse scattering in transmission electron microscopy (TEM), which quantifies the large-amplitude thermal vibrations of small molecular crystals (Eggeman *et al.*, 2013). The results of a series of brick wall stacked molecular crystals based on pentacene (TIPS-Pentacene and TMES-Pentacene), anthradithiophene (TESADT and diF-TESADT), or thienothiophene (C8-BTBT, C10-DNTT), (Illig *et al.*, 2016) show that large-amplitude thermal motions can be reduced, e.g., by using side chains attached along the long axis of their conjugated core to encapsulate the crystal structure with a large force constant. As an example, transient localization is closely related to the mobility anisotropy in single crystals, e.g. tetracene (Fig. 10(c)), in the form of intermolecular phonons (Bittle *et al.*, 2019). One mode (Mode II, bottom right in Fig. 10(d)) changes the shared crystal HOMO subtly and causes a localization along the high-mobility direction, whereas another (Mode III, top right in Fig. 10(d)) has a molecular bending motion which changes the HOMO significantly and causes a breakdown of the band structure along the high-mobility direction, as identified by polarized Raman spectroscopy and TEM. To date, the limitation of transport from thermal fluctuations in the transfer integrals (i.e. dynamic disorder) has already emerged in highly crystalline organic semiconductors with minimized, where the optimizations of crystal and device fabrications have efficiently eliminated the effects from static charge carrier traps and crystal domain boundaries (Chuan *et al.*, 2011; Tao *et al.*, 2013). The wafer-scale, large-area single crystalline thin films especially on thienothiophene-based and other molecules (Yamamura *et al.*, 2018; Zhou *et al.*, 2018; Jiang *et al.*, 2011) and their combinations may allow the in-depth studies of transport in crystals, i.e. transfer integral and polarization or dynamic disorder models.

Highly Disordered System With Hopping and Percolation

In amorphous or highly disordered semiconductors, charge transport mainly occurs by hopping or tunneling among localized states, and the most commonly used models are the variable range hopping model, (Mott, 1969; Vissenberg *et al.*, 1998a; Baranovskii *et al.*, 1997; Mott *et al.*, 1979) Bässler's Gaussian disorder model, (Coropceanu *et al.*, 2007; Bässler, 1993; Young, 1995;

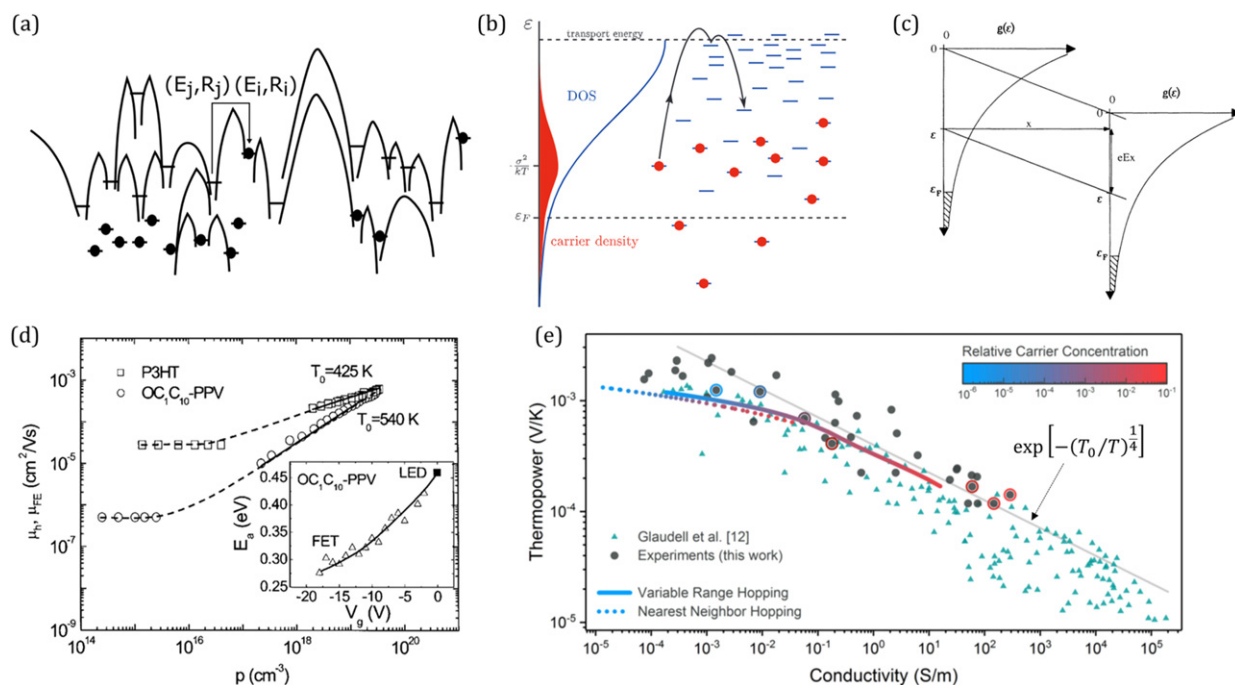


Fig. 11 Variable range hopping mechanisms. (a) A scheme of variable range hopping transport among localized states. (b) Schematic equilibrium energy distribution of carriers in a Gaussian DOS and a hopping event to transport level. The gray area is the DOS, the golden area represents the occupied states, and the black and white dots represent occupied and unoccupied states. (c) Field-dependent hopping. The electric field induces the inclination of the conduction levels and a higher concentration of shallower localized states available for electron hopping. The shaded area represents the occupied states (up to Fermi energy) in the mobility gap. (d) Mobility as a function of hole density p in a diode and FET for P3HT and OC₁C₁₀-PPV (experimental data in dots and hopping theories in lines). Inset: The activation energy of the mobility in the OC₁C₁₀-PPV OFET as a function of gate voltage (triangles), together with the activation energy of 0.46 eV as obtained from the diode at low densities (square). (e) Thermopower vs conductivity of doped disordered organic semiconductors. Gray full circles are experiments, green triangles are multisource experimental data, and colored lines are calculated with the analytical model parametric in carrier concentration (relative to the total DOS) as indicated in the legend. The VRH model clearly reproduces the $-1/4$ power-law relationship observed experimentally (gray line). (a) Adapted with permission from Marinov, O., *et al.*, 2020. Variable-range hopping charge transport in organic thin-film transistors. *Phys. Rep.* 844, 1–105. (b) Marianer, S., *et al.*, 1992. Effective temperature of hopping electrons in a strong electric field. *Phys. Rev. B* 46, (13100). (c) Tanase, C., *et al.*, 2003a. Unification of the hole transport in polymeric field-effect transistors and light-emitting diodes. *Phys. Rev. Lett.* 91. Abdalla, H., *et al.*, 2017. Range and energetics of charge hopping in organic semiconductors. *Phys. Rev. B* 96, 241202.

Schmechel, 2002) and the percolation model (Coropceanu *et al.*, 2007; Brotherton, 2013a; Lee *et al.*, 2011). Some of them are also considered Organic semiconductors in a polycrystalline state.

In disordered organic solids, charge transport generally occurs by hopping between localized states. The basic hopping theory in inorganic semiconductors at low temperatures assumes that the jump rate is Miller-Abrahams-like, which assumes that an uphill hop is characterized by a balance factor, $\exp\left(-\frac{E_a}{k_B T}\right)$ with E_a as the energy offset, and a downhill hop is temperature independent and is not impeded by an energy-matching condition (Miller *et al.*, 1960). The hopping rate between adjacent occupied site i and unoccupied site j separated in energy by E_{ij} (the energy difference between site i and site j) and in distance by R_{ij} (the distance between site i and site j) is given by the Miller-Abraham expression:

$$W_{ij} = \nu_0 \exp(-2\alpha R_{ij}) \times \begin{cases} \exp\left(-\frac{E_{ij}}{k_B T}\right) & E_{ij} > 0 \\ 1 & E_{ij} < 0 \end{cases} \quad (12)$$

where ν_0 is a typical phonon frequency factor and α^{-1} is the localization radius of a charge carrier. This mechanism is schematically shown in Fig. 11(a).

As an extension of this hopping mechanism, Mott introduced a variable range hopping (VRH) concept (Mott *et al.*, 1979), whereby the charge carrier may either hop over a small distance with a high activation energy or hop over a long distance with a low activation energy, in a constant density of localized states. The temperature dependence of mobility is derived as:

$$\mu \propto \exp\left[-\left(\frac{T_0}{T}\right)^{\frac{1}{n+1}}\right] \quad (13)$$

where T_0 is a parameter inversely proportional to the density of states at the Fermi level and n is the dimensionality of the system ($n = 1, 2, 3$). By combining the VRH concept with the percolation theory (Ambegaokar *et al.*, 1971) and a transistor model, Vissenberg and Matters formulated the field-effect mobility in amorphous organic FETs, in the framework of the exponential density of tail states (Vissenberg *et al.*, 1998b). This model successfully explains the temperature and gate voltage dependence of FET mobility taken from pentacene and poly(thienylene vinylene) (PTV) (Vissenberg *et al.*, 1998b). Moreover, the concept of activation to a transport level applies to a broad class of DOS, as has been shown by Baranovskii *et al.* (Baranovskii *et al.*, 1997; Baranovskii, 2014).

Based on VRH, the Gaussian distribution of localized states was further considered in the charge transport model and proposed by Bässler for disordered organic systems (Bässler, 1993; Lu *et al.*, 2016). This is schematically shown in Fig. 11(b). He assumed that the carriers are not polaronic and that the activation energy of the charge transport is dominated by both an energetic and positional disorder of the hopping sites. The hopping rates are described by the Miller-Abrahams formalism (Eq. 12) and the density of states (DOS) for localized states is assumed in Gaussian distribution: $N(E) = \frac{N_0}{\sqrt{2\pi}\Delta E} \exp\left[-\frac{(E-E_0)^2}{2\Delta E^2}\right]$, where N_0 is the characteristic band DOS (usually 10^{21} cm^{-3}), ΔE is the width of the Gaussian density of states (usually below 0.2 eV), and E_0 is the center of the DOS. Monte Carlo simulations based on the equation above revealed that charges injected within a Gaussian DOS relax to dynamic equilibrium energy $-\Delta E/k_B T$ below the center of the DOS, while the energy required to the transport level is $-5\Delta E/9k_B T$. The difference between the two energies results in a non-Arrhenius temperature dependence of mobility $\propto \exp[-(2\Delta E/3k_B T)^2]$. The mobility dependent on temperature and the electric field is given by,

$$\mu = \mu_0 \exp\left[-\left(\frac{2\Delta E}{3k_B T}\right)^2\right] \times \begin{cases} \exp\left[C\left(\left(\frac{\Delta E}{k_B T}\right)^2 - \Sigma\right)\epsilon^{1/2}\right] & \Sigma \geq 1.5 \\ \exp\left[C\left(\left(\frac{\Delta E}{k_B T}\right)^2 - 2.25\right)\epsilon^{1/2}\right] & \Sigma < 1.5 \end{cases} \quad (14)$$

where μ_0 is the mobility at infinite absolute temperature and at zero fields, C is an empirical constant, and Σ is the degree of the positional disorder. In many disordered organic materials, the Poole-Frenkel (PF)-type field dependence of mobility in Eq. (14), $\mu \propto \exp[\gamma\sqrt{\epsilon}]$, has been observed experimentally at high fields ($\epsilon > 10^6 \text{ V/cm}$) (Abkowitz, 1992; Schein *et al.*, 1989). The effect of the electric field ϵ on the carrier mobility μ is due to the effect of the field on the energy landscape of the system and concomitantly on the hopping transition rates dependent on the energies of the localized states (Baranovskii, 2018), i.e. adding an extra term $q\epsilon R_{ij}$ into the energy term E_{ij} in Eq. 12. Also, as the electric field enhances the number of sites available for charge transport at $T = 0$ in the field direction (Fig. 11(c)) (Marianer *et al.*, 1992), the high field dependent mobility could be equivalently treated as part of effective temperature to replace T in Eq. 13: $T_{\text{eff}}(T, \epsilon) = \left[T^\beta + (\gamma q \epsilon \alpha / k_B)^\beta\right]^{1/\beta}$, where β and γ are constant (Marianer *et al.*, 1992).

The above VRH theories give how carrier mobility is affected by the factors of temperature and electric field. The aforementioned work by Vissenberg and Matters is the hopping percolation model in an exponential DOS, which yields an expression for the conductivity and mobility as a function of the charge carrier density n and the temperature:

$$\mu = \frac{\sigma_0}{q} \left(\frac{(T_0/T)^4 \sin(\pi T/T_0)}{(2\alpha)^3 B_c} \right)^{T_0/T} n^{T_0/T-1} \quad (15)$$

where σ_0 is a prefactor for the conductivity, α is the effective overlap parameter between localized states, T_0 is a measure of the width of the exponential density of states, and B_c is the critical number for the onset of percolation. The hopping model explains well the transition of carrier mobility from a rather low value in OLEDs with low carrier density to a high value in OFETs with high carrier

density, which are made of P3HT and OC1C10-PPV (Tanase *et al.*, 2003a; Pasveer *et al.*, 2005). The theory well explains the experimental results that the carrier mobility μ depends on the carrier concentration n at large n (e.g. in OFET) but becomes n -independent at small n (e.g., in OLED) as exemplified in Fig. 11(d) (Tanase *et al.*, 2003a). In addition, the thermal power measurements based on organic semiconductors also confirm VRH rather than nearest neighbor hopping (NNH) dominates transport at various temperatures, as the VRH model produces a kinked shape of the conductivity dependence that reproduces the experimentally observed $-1/4$ power law at high conductivities while flattening out at lower conductivities (Fig. 11(e)) (Abdalla *et al.*, 2017).

Bässler's Gaussian disorder model (GDM) assumes independent site energies and does not involve any special correlations. However, Novikov *et al.* observed that a large-scale spatial correlation, due to charge dipole interactions, provided a significant contribution to the site energy (Novikov *et al.*, 1995), and the length-scale of correlation is greater than the inter-site distance. They proposed the correlated disorder model (CDM), in which the Poole-Frenkel field dependence is a universal feature that extends to lower electric fields (Novikov *et al.*, 1998), while the GDM model shows PF behavior only over a very narrow range at high fields. Using the CDM hopping model, the temperature and field- dependent mobilities of LED devices have been well explained (Tanase *et al.*, 2003b).

Unified Descriptions for Charge Transport

The above theories predict different relations between carrier mobility and temperature or carrier concentrations. Based on the general consensus that electronic states near the edge of the density of states are more localized than those near the center (exemplified in Fig. 12(a)), the various transport mechanisms could be unified by the description of generalized Einstein relation (GER) that assumes the Gaussian distributed density of states (DOS) and the attenuated delocalization at the electronic states near band edge or the energy gap (Liu *et al.*, 2017a; Xu *et al.*, 2011).

In a single crystalline, non-degenerate semiconductor, the Einstein relation between the diffusion coefficient D and mobility μ takes its classical form: $D/\mu = k_B T/q$. In disordered semiconductors, the ratio of diffusion coefficient to mobility becomes a function of carrier concentration in the GER: (Roichman *et al.*, 2002)

$$\mu = \frac{qD}{n(E_F, T)} \frac{\partial n(E_F, T)}{\partial E_F} \quad (16)$$

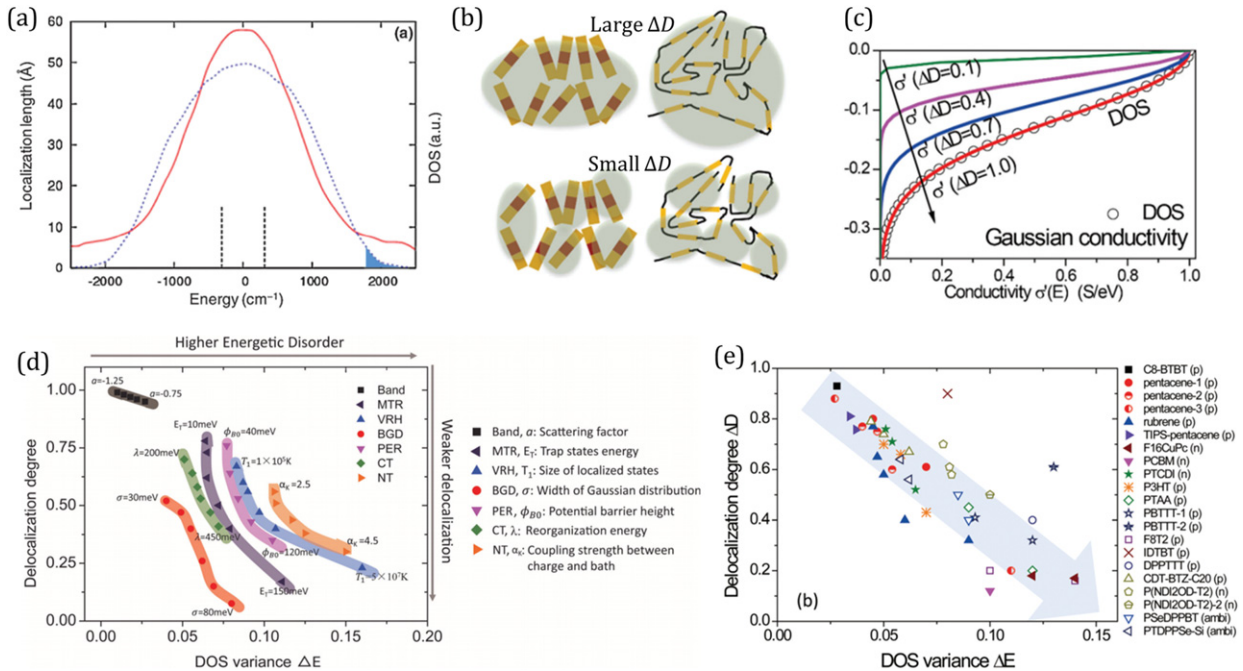


Fig. 12 Unified descriptions for charge transport. (a) Localization length (red solid line) and DOS (blue dotted line) for 6,13-bis(triisopropylsilyl)ethynyl pentacene (TIPS-P). (b) Schematic representations of the delocalization of carriers in the states with high energies near the DOS center (upper) or in the states with low energies near the band edge (lower). The shades are illustrative of the delocalization area. (c) Normalized microscopic conductivity $\sigma'(E)$ as a function of energy for different degrees of delocalization ΔD (ΔE is fixed). (d) The values of ΔD and energy dispersion parameter ΔE are plotted for various transport models with the corresponding key parameters. (e) The values of ΔD and ΔE are plotted for different semiconductors. Adapted with permission from Liu, C., *et al.*, 2017a. A unified understanding of charge transport in organic semiconductors: The importance of attenuated delocalization for the carriers. Mater. Horiz. 4, 608–618. Chang, J.F., *et al.*, 2011a. Hall-effect measurements probing the degree of charge-carrier delocalization in solution-processed crystalline molecular semiconductors. Phys. Rev. Lett. 107.

where n is the total carrier concentration and E_F is the Fermi energy. In disordered organic semiconductors, Eq. (16) should be used under the assumption that mobility is a function of energy E , by assuming a certain hopping probability (Li *et al.*, 2014). The overall mobility should reflect the features of weak bonding, degeneration, and defect-abundant of organic semiconductors and are given by:

$$\mu = \frac{\sigma}{qn} = \frac{q \int_{-\infty}^{+\infty} \sigma'(E) \left[-\frac{\partial f(E)}{\partial E} \right] dE}{\int_{-\infty}^{+\infty} N(E) f(E) dE} \quad (17)$$

The overall carrier density n is: $n = \int_{-\infty}^{+\infty} N(E) f(E) dE$ with a narrow Gaussian DOS (Xu *et al.*, 2011; Roichman *et al.*, 2002; Khim *et al.*, 2016) and Fermi-Dirac distribution is $f = 1 / \left\{ 1 + \exp \left[\frac{(E - E_F)}{kT} \right] \right\}$. The overall conductivity σ for all the carriers is calculated with Kubo-Greenwood integral (Mott *et al.*, 1979; Xu *et al.*, 2011). Instead of the ME and MTR models that simply assume a constant μ above ME and a near-zero μ below ME, the microscopic conductivity of electronic states (σ') reflects the attenuation of conductivity from the DOS center to the edge (Mott *et al.*, 1979; Xu *et al.*, 2011):

$$\sigma'(E) = \frac{\sigma_0}{\sqrt{2\pi(\Delta D \cdot \Delta E)}} \exp \left[-\frac{(E - E_0)^2}{2(\Delta D \cdot \Delta E)^2} \right] \quad (18)$$

where $\sigma_0 = N_C q \mu_0 / 2$ is the characteristic conductivity and μ_0 is the characteristic mobility.

The ΔE characterizes the degree of energy dispersion determined by the static or structural factors, including crystallinity and electronic interactions/coupling among neighboring molecules. The ΔD (≤ 1 , no unit) characterizes the degree of delocalization for electronic states near the edge of DOS (near HOMO or LUMO levels): when $\Delta D = 1$, the delocalization degree is the same for the whole DOS and the shape of $\sigma'(E)$ is only determined by the DOS (Fig. 12(b,c)) and the macroscopic charge transport properties would ideally follow the first-principles evaluations (Jiang *et al.*, 2016; Wang *et al.*, 2010); when $\Delta D < 1$, a small ΔD means severely attenuated $\sigma'(E)$ from the center of DOS (extended states) to the edge (localized states), with thus severely localized tail states. The localization could be induced by microscopic voids, grain boundaries, polymeric twisting, dynamic disorders (lattice vibrations), or chemical impurity scattering (Fig. 12(b)). By varying ΔE (usually below 0.2 eV) (Sato *et al.*, 2022) and ΔD (from 0 to 1), GER can well describe most charge carrier mobility dependence on temperature as predicted by the above-mentioned models with different views of microscopic dynamic processes (Fig. 12(d)) and experimental data of mobility for various semiconductors (Fig. 12(e)), (Coropceanu *et al.*, 2007; Brotherton, 2013a; Seto, 1975; Levinson *et al.*, 1982; Voutsas, 2003; Horowitz, 1998a; Le Comber *et al.*, 1970; Yin *et al.*, 2011; Marcus, 1956, 1993; Yavuz *et al.*, 2015a; Asadi *et al.*, 2013; van der Kaap *et al.*, 2016; Mott, 1969; Vissenberg *et al.*, 1998a; Baranovskii *et al.*, 1997; Mott *et al.*, 1979; Bässler, 1993; Young, 1995; Schmechel, 2002; Lee *et al.*, 2011) including the band-to-hopping transition (i.e., $d\mu/dT < 0$ to $d\mu/dT > 0$) (Sakanoue *et al.*, 2010; Podzorov *et al.*, 2004; Minder *et al.*, 2012).

Besides GER, where the two parameters critically determine the temperature-dependent mobility, Fornari *et al* demonstrate that the steady state charge mobility in the limit of low charge density and low field ultimately depends on only two parameters: an effective structural disorder and an effective electron-phonon coupling, weighted by the size of the monomer (Fornari *et al.*, 2017). The model helps explain the experimental observation of universal temperature dependence of the mobility determined by a single experimental parameter.

Notice that the classic scenario of “band-like transport” and “hopping” transport illustrated in Fig. 3 has no clear boundary. Basically, when the electronic coupling between the neighboring sites for charges to drift or diffuse is very strong, “band-like” transport is mainly considered; when the localization effect is strong, e.g., polarons are self-limited among discrete sites, thermal-activated hopping is mainly considered. Nevertheless, the “band-to-hopping” transitions have been experimentally observed in many organic semiconductors and explained in various models (Liu *et al.*, 2017a; Xu *et al.*, 2011; Wang *et al.*, 2007; Ortmann *et al.*, 2009; Wang *et al.*, 2013; Yamashita *et al.*, 2014; Yavuz, 2017; Giannini *et al.*, 2018).

The Macroscopic View – Mobility in Electronic Devices

For electronic devices, carrier mobility characterizes how conductive the semiconductor channel is. In a segment of conductor or a metal-semiconductor-metal structure, the local current density is dependent on μ :

$$J = \sigma \epsilon = nq\mu\epsilon \quad (19)$$

where σ is conductivity, n is the local carrier density, q is the elementary charge, μ is characteristic carrier mobility, ϵ is the local drift electric field.

Metal-semiconductor-metal Structure

The metal-semiconductor-metal structure is usually referred to as an organic diode, although there is no well-defined p - n junction. In the Ohmic conduction regime, the injected carriers are much fewer than the intrinsic carrier density and the carrier density and conductivity are uniform. The carrier mobility could be measured by using Eq. (3), i.e., Ohm’s law to estimate the

carrier mobility if the carrier density is known. When the injection is strong so that a space charge limit region is built, the ideal space charge limited current (SCLC) (Blakesley *et al.*, 2014; Pope *et al.*, 1999) dominates with the dependence on μ in the form of Mott-Gurney regime:

$$J = \frac{9}{8} \epsilon_0 \epsilon \mu \frac{V^2}{d^3} \quad (20)$$

If the semiconductor is with a single level trapping states or the trapping states are distributed narrowly so that they could be approximated as a single level, the trap-filled limited (TFL) SCLC could be expressed as:

$$J = \frac{9}{8} \theta \epsilon_0 \epsilon \mu \frac{V^2}{d^3} \quad (21)$$

where $\theta = n_{\text{free}}/n_{\text{total}} = \frac{N}{N_t} \exp\left(\frac{E_t}{kT}\right)$ is the ratio between the free carrier density and the trapped carrier density. N_t is the total trap density, N is the density of transport sites available for conduction. For electron-only and hole-only transport, N is the effective density of states in the conduction band (N_C) and valence band (N_V), respectively. E_t is the energy of the shallow trap with respect to the band edge (Haneef *et al.*, 2020).

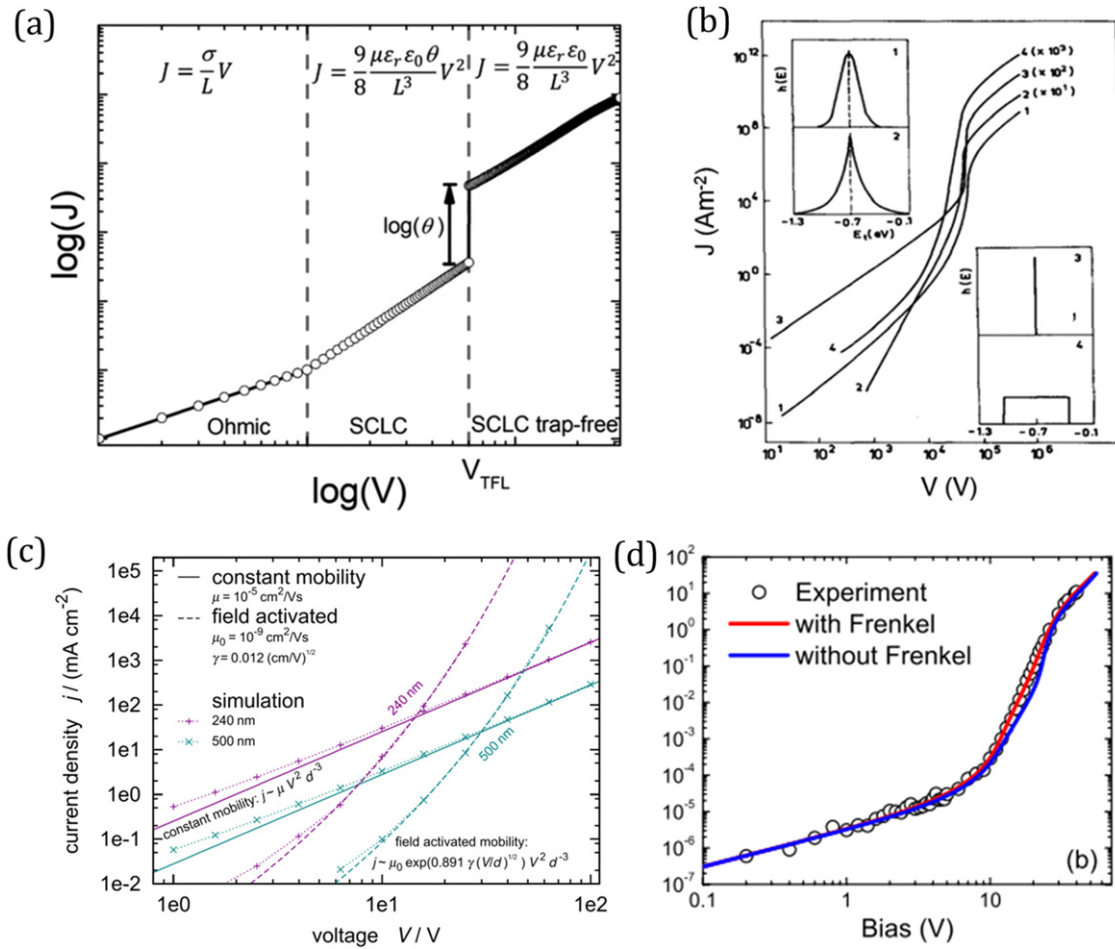


Fig. 13 *I-V* characteristics of organic diodes. (a) Typical current-voltage characteristics from SCLC measurements for a discrete distribution of shallow traps characterized by the Ohmic, SCLC, and SCLC trap-free regimes. (b) Calculated I - V characteristics for various distributions of trapping states as shown in the insets (1) Gaussian distribution, (2) double exponential distribution, (3) discrete distribution, and (4) uniform distribution, all with the same energy center. (c) Simulated and analytically calculated I - V characteristics of single carrier devices at two thicknesses. Solid lines: Mott-Gurney law for constant mobility; dashed lines: A field-activated mobility. Symbols (connected by dotted lines): Drift-diffusion simulations of p - i - p hole-only devices with the same mobility models. (d) Comparing the I - V data with theory for an electron-only polyphenylene vinylene PPV device including the Frenkel effect (red line), and neglecting the Frenkel effect (blue line). Adapted with permission from Nešpůrek, S., *et al.*, 1990. Spectroscopy of local states in molecular materials using space-charge-limited currents. *Int. J. Radiat. Appl. Instrum. Part C Radiat. Phys. Chem.* 36, 3–12. Widmer, J., *et al.*, 2013. Electric potential mapping by thickness variation: A new method for model-free mobility determination in organic semiconductor thin films. *Org. Electron.* 14, 3460–3471. Zhang, X.G., *et al.*, 2012. Theory of space charge limited currents. *Phys. Rev. Lett.* 108, 266602.

If the semiconductor is with an exponential distribution of trapping states, the SCLC is:

$$J = N_C q \mu \left[\frac{\epsilon_0 \epsilon \delta}{(\delta + 1) N_t} \right]^\delta \left(\frac{2\delta + 1}{\delta + 1} \right)^{\delta+1} \frac{V^{\delta+1}}{d^{2\delta+1}} \quad (22)$$

where by the $\delta = T/T_0 - 1$ and T_0 is the characteristic temperature with $k_B T_0$ as the width of the energy tail states. For more general cases, the semiconductor is with an arbitrary distribution of trapping states and the conductivity could be roughly expressed by $J = n(n/n_{t0})^{\delta-1} q \mu_0 \epsilon (\epsilon/\epsilon_{t0})^{\kappa-1} = A n^\delta q \mu_0 \epsilon^\kappa$, where n is the carrier density, q is the elementary charge, μ_0 is characteristic carrier mobility, ϵ is the drift electric field, n_{t0} and ϵ_{t0} are characteristic carrier density and drift electric field mainly related to bulk traps of interfacial states, δ and κ are power factors. The SCLC current is expressed by:

$$J = A \left(\frac{\delta}{\delta + \kappa} \right)^\delta \left(\frac{2\delta + \kappa}{\delta + \kappa} \right)^{\delta+\kappa} \frac{\epsilon^\delta}{q^{\delta-1}} \mu_0 \frac{V^{\delta+\kappa}}{d^{2\delta+\kappa}} = Q_0 \mu_0 \frac{V^\alpha}{d^\beta} \quad (23)$$

where Q_0 is the charge density factor, α is the charge transport factor, and β is usually $2\alpha - 1$. Such a descriptive formula can summarize general conduction mechanisms in on-state diodes including Ohmic conduction, SCLC, trap-filled SCLC, the transitions between Ohmic and SCLC, and vacuum diodes (Liu *et al.*, 2021a).

The typical current-voltage characteristics of organic diodes are illustrated in Fig. 13(a). The characteristics could be affected by the distribution of trap states (Fig. 13(b)), field-activated mobility (Eq. 13(c) and Eq. 21). The filling of trapping states and the Frenkel effect (the lowering of the ionization energy by the electric field) take the critical role in determining the slope of sharply rising IV curves (Fig. 13(d)). In these cases, the impact of carrier mobility becomes secondary, until all trap states are filled and the Mott-Gurney regime (Eq. 18) takes the place of the power-law rise in the IV curves (Zhang *et al.*, 2012). Nevertheless, carrier mobility can be extracted by measuring the potential and IV curves of organic diodes with varied thicknesses, as shown by Widmer *et al.* (2013).

Organic Field-Effect Transistors

The current-voltage relations and structure of organic field-effect transistors (OFETs) or organic thin-film transistors (OTFTs) are exemplified in Fig. 14 (Wang *et al.*, 2012). Above threshold voltage V_{th} , OFETs would ideally behave following three basic, main assumptions concerning the fields within the three terminals: (a) *Vertical field*. A vertical electric field is formed inside a series of parallel-capacitor gapped by the source/drain/channel terminal and the gate electrode. The carrier concentration at any position x in the channel follows the $n(x) = \frac{1}{q} C_i V_G - V(x) - V_{th}$ and the overall increased carrier concentration from V_{G1} to V_{G2} in the channels would follow $\Delta n = \frac{1}{q} C_i V_{G2} - V_{G1}$ above the threshold; (b) *Lateral field*. A lateral electric field is formed between the source and drain electrodes (in the linear and non-linear regime) or the pinch-point ($V(x) = V_G$ in the saturated regime). The local electric field between any two points x_2 and x_1 within this region is $E_x = \frac{1}{L}(V_{x2} - V_{x1})$ and the minimum absolute voltage is near the source as V_0

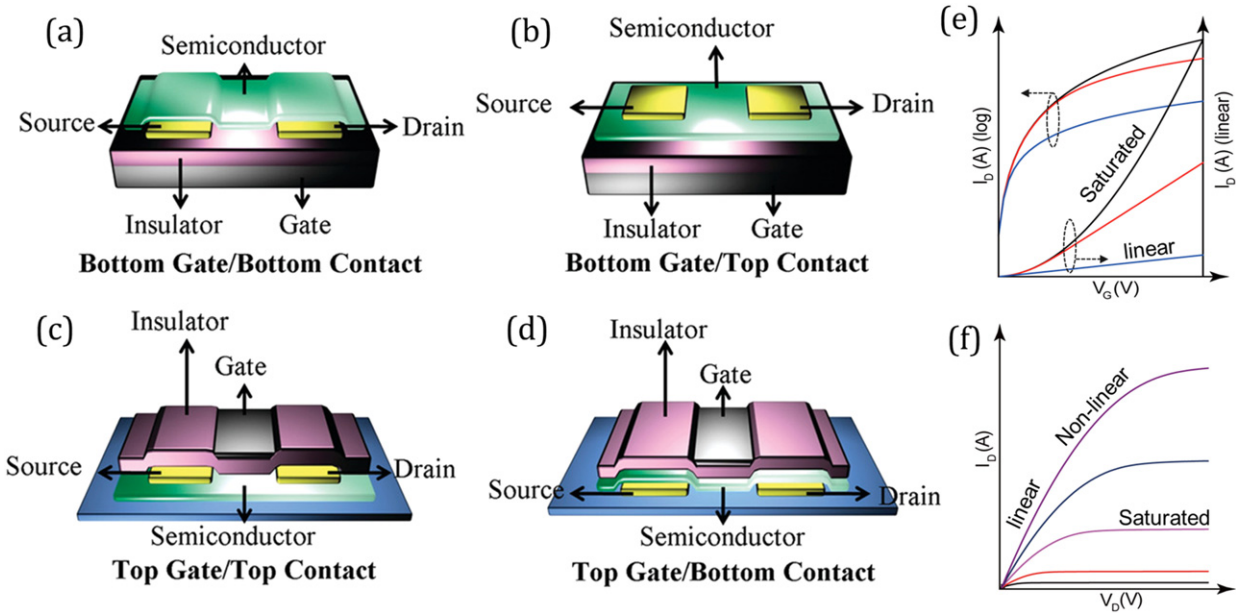


Fig. 14 Structures and IV characteristics of organic transistors. (a-d) Four types of OFETs: (a) bottom gate/bottom contact, (b) bottom gate/top contact, (c) top gate/top contact, and (d) top gate/bottom contact. (e) Typical transfer curves and (f) output curves of OFETs. Adapted and modified from Tengzhou, Y., *et al.*, 2019. Understanding, optimizing, and utilizing nonideal transistors based on organic or organic hybrid semiconductors. *Adv. Funct. Mater.* 30, 1903889. Wang, C., *et al.*, 2012. Semiconducting π -conjugated systems in field-effect transistors: A material odyssey of organic electronics. *Chem. Rev.* 112, 2208–2267.

(ideally V_0 should be 0); (c) *Two fields*. In the linear regime, V_G only determines the vertical field and V_D only determines the lateral field. In the non-linear or saturated regime, both V_G and V_D simultaneously affect the vertical and lateral fields. The vertical field is always much larger than the lateral field within the accumulation channel (not including the depletion region).

Based on the above assumptions, the ideal current-voltage relation in FETs or TFTs above threshold is (Brotherton, 2013b):

$$I_D = WC_i \left(V_G - V_{th} - \frac{V_D}{2} \right) \times \mu \frac{V_D}{L} \quad (24)$$

for any V_G above the threshold V_{th} and below V_D (V_G above the threshold voltage V_{th} plus V_D). The device parameters include channel width (W), channel length (L), and capacitance per unit area (C_i), scanning parameters include drain voltage (V_D) and gate voltage (V_G), measured parameter is drain current (I_D), and extracted parameters include field-effect mobility μ_{lin} and μ_{sat} and threshold voltage V_{th} . Compact models of OFETs have been developed (Kim *et al.*, 2014; Li *et al.*, 2010). The linear ($V_G \gg V_D$) or saturated ($V_G \leq V_D$) regime is usually approximated as:

$$I_D = \frac{W}{L} \mu_{lin} C_i (V_G - V_{th}) V_D \quad (25)$$

$$I_D = \frac{W}{2L} \mu_{sat} C_i (V_G - V_{th})^2 \quad (26)$$

for any V_G above the threshold V_{th} . However, the above assumptions for an ideal transistor are hardly satisfied in a real transistor, requiring constant field-effect mobility μ , Ohmic contacts, the single polarity of carrier (electron or hole transport only), minimal bulk and interfacial defects (single crystalline semiconductor and clean dielectric interface), precise determination of the geometric parameter W and L , and constant C_i and V_{th} .

For ambipolar transistors with electron and hole transport (Zaumseil *et al.*, 2006; Anthopoulos *et al.*, 2004), both the carrier mobility contributes to the current:

$$I_D = \frac{W}{L} C_i \left[\mu_n \left(V_G - V_{th,n} - \frac{V_D}{2} \right) + \mu_p \left(V_G - V_{th,p} - \frac{V_D}{2} \right) \right] V_D \quad (27)$$

where μ_n and μ_p refer to the carrier mobility of electrons and holes, and $V_{th,n}$ and $V_{th,p}$ refer to the threshold voltage of n -type and p -type channel current, respectively.

Hall Effect Devices and Thermal-Electric Bar

Note that the measurement of carrier mobility of field-effect transistors relies on the estimation of carrier concentration (per unit area), which is assumed to be $n = C_i (V_G - V_{th})/q$. The estimation could lead to significant errors in extracting carrier mobility. In comparison, Hall effect measurement can directly measure the carrier concentration from the Hall-effect coefficient $R_H = 1/nq$, if

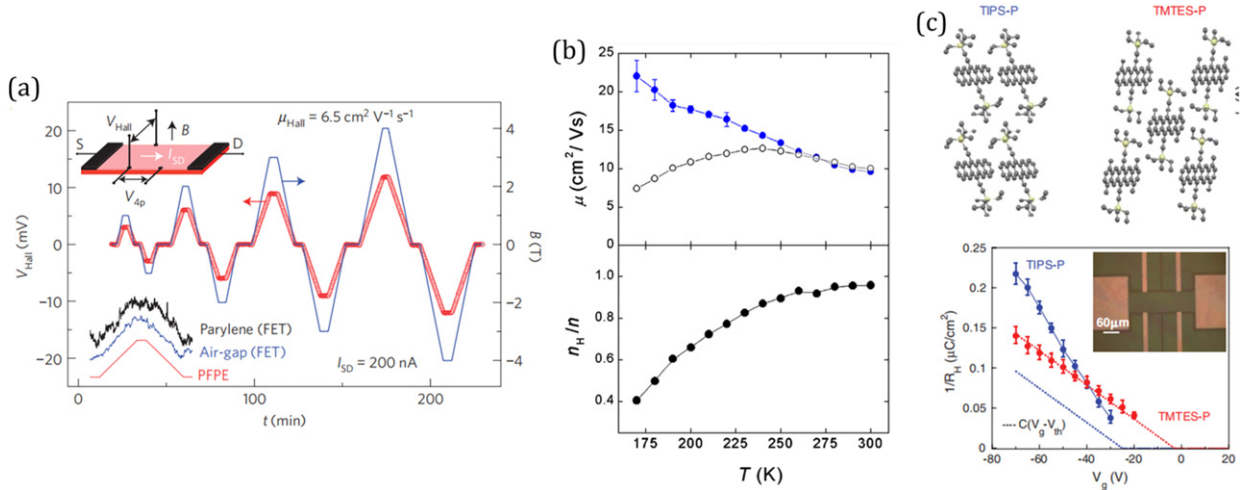


Fig. 15. Structure and I/V characteristics of organic Hall effect devices. (a) Scheme of Hall-effect measurements. The two types of charge carriers (both holes) in organic semiconductors with disorder: a coherent band-like hole moving in delocalized states (solid red circle) and a hopping hole moving in localized tail states (open blue circle). (b) (top) Temperature-dependent Hall mobility μ_H (solid circles) and the mobility extracted from the conductivity using the density n calculated from the gate-channel capacitance (open circles); (bottom) temperature-dependent ratio of Hall carrier density n_H to the density n . (c) (top) Single-crystal structure of TIPS-P and TMES-P with the one- and twodimensional stacking of molecules can clearly be seen; (bottom) inverse Hall coefficient $1/R_H$ and gate-induced charge density $Q = C_i (V_G - V_{th})$ as a function of gate voltage. Adapted with permission from Chang, J.F., *et al.*, 2011A. Hall-effect measurements probing the degree of charge-carrier delocalization in solution-processed crystalline molecular semiconductors. *Phys. Rev. Lett.* 107. Podzorov, V., *et al.*, 2005. Hall effect in the accumulation layers on the surface of organic semiconductors. *Phys. Rev. Lett.* 95, 226601. Yi, H., *et al.*, 2016. Charge carrier coherence and Hall effect in organic semiconductors. *Sci. Rep.* 6, 1–11.

diffusive transport in delocalized states (i.e., band transport with long mean-free path) rather than incoherent thermally activated hopping (or variable range hopping) dominates the charge transport (Podzorov *et al.*, 2005; Lee *et al.*, 2013). Therefore, the Hall-effect mobility is the microscopic carrier mobility. Examples of Hall effect measurement on rubrene crystals are shown in Fig. 15. Notice that the hall effect mobility and carrier density can significantly deviate from that measured by transistor extraction methods (Fig. 15(b)) (Podzorov *et al.*, 2005; Takeya *et al.*, 2005). This is also evidenced in the different signals of 6,13-bis(triisopropylsilyl)ethynyl pentacene (TIPS-P) and 1,4,8,11-tetramethyl-6,13-triethylsilyl ethynyl pentacene (TMTEs-P) in Fig. 15(c), because the localization length of TMTEs-P is long enough that the majority of charges experience a semiclassical Lorentz force while in TIPS-P a significant portion of charges remain too strongly localized to contribute to the Hall voltage (Chang *et al.*, 2011a).

The thermoelectric Seebeck effect, generally evaluated by the Seebeck coefficient (also referred to as thermopower), can be obtained using the equation $S = \Delta V / \Delta T$. The Seebeck voltage (ΔV) and the corresponding ΔT are the potential drop and temperature difference between two ends of a sample with a thermal gradient. The Seebeck coefficient is determined by the concentration and energy-dependent conductivity of charge carriers. Thus, provides information on the energetics of dominant charge transport processes and the average transport energy of carriers (Lu *et al.*, 2016).

Mobility in Different Devices

The carrier mobility measured in diodes and transistors made with the same organic semiconductors are usually different, as charge transport are highly dependent on charge density. Charge density in organic diodes is close to the intrinsic charge carrier density if it is in the Ohmic conduction regime or higher if in the space charge limited conduction regime (in the non-degenerate or degenerate state 10^{14} to 10^{16} cm^{-3}), whereas charge density in organic transistors is much higher due to the accumulation by the gate field (in the degenerate state with 10^{18} to 10^{20} cm^{-3}). This difference leads to much higher mobility values in organic transistors as compared with those in organic diodes, up to several orders of magnitude (Tanase *et al.*, 2003a). In comparison, the mobility of Hall-bar devices also made in the transistor configurations is in the same order of magnitude as those obtained in transistors. In particular, can be equal if the coherent charge transport dominates, as discussed above.

Measurement of Carrier Mobility

Measurement Methods

The carrier mobility of organic semiconductors has been usually measured by TOF, SCLC, FET characterizations, and Hall effect measurements (Podzorov *et al.*, 2005; Chang *et al.*, 2011b; Kokil *et al.*, 2012). Early experimental methods to determine carrier mobilities by electric transport methods include the equilibrium charge carrier extraction method (Arthur *et al.*, 1955; Bray, 1955; Arlauskas *et al.*, 2000; Juska *et al.*, 2000), drift current methods under limited range conditions (van de Craats *et al.*, 1996; Gelinck *et al.*, 1996; Hoofman *et al.*, 1998), the conductivity/concentration (σ/n) method, (Podzorov *et al.*, 2004; Nguyen *et al.*, 1994; Brütting *et al.*, 1995) the surface acoustic-electric traveling wave method (Karl *et al.*, 2000), and etc (Karl, 2003). These methods have been less employed as compared to FET characterizations which directly connect the mobility value to the functional circuits. Nevertheless, the *mobility* as the drift velocity in a unit electric field is the basis of all the *mobilities*, as stated below.

The measured mobility values obtained by TOF or SCLC measurement on the metal-semiconductor-metal structures are usually several orders of magnitude lower than those obtained from OFET measurements with the same organic materials, although the TOF mobilities can be higher if the charges being transported are in excited states. This is because the mobility in organic semiconductor strongly depends on the charge carrier density or concentration (as discussed below) and OFET measurements are undertaken with dense carriers accumulated in a nanometer-scale thin layer, (Shehu *et al.*, 2010; Kiguchi *et al.*, 2003) resulting in relatively high charge carrier densities (10^{18} to 10^{19} cm^{-3}) or carrier concentration (10^{11} to 10^{12} cm^{-2}) (Shuttle *et al.*, 2010). According to SCLC, it is possible to track the potential evolution on thickness or channel length dependence of current to yield the spatial distribution of the electric field and charge carrier density so that carrier mobility could be estimated (Widmer *et al.*, 2013).

In transistors or Hall-effect measurements, the carrier mobility is generally extracted by measuring the conductance G and assessing the carrier concentrations n (cm^{-2} or cm^{-3}). In transistors, the FET mobility in a certain measurement window is calculated by estimating the carrier concentration n as $\mu_{\text{FET}} = \frac{L}{Wq} \frac{\Delta C}{\Delta n}$ (for linear or non-saturated regime). The measured mobility would be strongly affected by the semiconductor-dielectric interface and the metal-semiconductor interface (Wen *et al.*, 2011; Dong *et al.*, 2013), which may affect the carrier concentration n , drift field E_x , and thus extraction of device mobility μ_{FET} . The measured μ_{FET} could be affected by broadening of DOS due to interface-induced states or dipoles, (Richards *et al.*, 2008; Yogeve *et al.*, 2011) interface-induced donor-like or acceptor-like states that affect carrier concentrations (Khim *et al.*, 2016; Lampert *et al.*, 2018; Marinkovic *et al.*, 2012; Liu *et al.*, 2013) or act as scattering centers (Schaffroth *et al.*, 2019), organic semiconductor layer numbers (Jiang *et al.*, 2011; Zhang *et al.*, 2016; Wang *et al.*, 2016, 2018a; Liu *et al.*, 2015a; Yang *et al.*, 2018; Tal *et al.*, 2005), and etc. The above transport models could be combined with the interfacial effects near the dielectrics due to the gate field (Dinelli *et al.*, 2004). However, in many cases, values of *device mobility* measured in devices (especially FETs) are far from the intrinsic transport properties in semiconducting channels, because the evaluation of n (and also E_x) can be easily affected by the electrode-semiconductor interfaces, and thus it raises the complexity in understanding, interpreting, and comparing μ_{FET} . The evaluation of carrier concentrations is based on the parallel-capacitor assumption $n = C_i(V_G - V_{\text{th}})/q$ with fixed V_{th} but it could be seriously

Table 2 Comparison of extraction method for carrier mobility in FETs. (Yang *et al.*, 2019)

	Scanning	Operation regime	Voltages	Contact resistance R_C	Key equations	References
FET method	Transfer	Linear / saturated	$V_{S0} = V_S$; $V_{D0} = V_D$	$R_C \sim 0$	$\mu_{lin} = \frac{L}{WC_i V_D} \left(\frac{\partial I_D}{\partial V_G} \right)$ for linear, $\mu_{sat} = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_D}}{\partial V_G} \right)^2$ for saturated	(Schroder, 2006)
TLM	Transfer	Linear	$ V_D < V_G $	Constant of L	$\mu_{TLM} = \frac{\partial g_{ch}}{\partial V_G}$, $g_{ch} = \left(\frac{\partial R_{ON} \cdot W}{\partial L} \right)^{-1}$	(Minari <i>et al.</i> , 2006)
Y-function	Transfer	Linear	$ V_D < V_G $	Constant of V_G	$\mu_0 = -\frac{\left(\frac{\partial Y}{\partial V_d} \right)^2 L}{WC_i V_d}$, $Y = \frac{I_d}{\sqrt{g_m}}$, $g_m = \frac{\partial I_d}{\partial V_g}$	(Xu <i>et al.</i> , 2010)
Hall-effect	Transfer	Linear	$ V_D < V_G $	No assumption	$\mu_H = \frac{1}{B} \frac{U_H}{V} \left(\frac{L}{W} \right)$	(Podzorov <i>et al.</i> , 2005)
G-function	Output	Linear / non-linear	$ V_D < V_G $	Decreases with $ V_D $	$\mu = -\frac{2}{C_L} \frac{\partial G}{\partial V_d}$, $G = \frac{\partial I_d}{\partial V_d}$, $C_L = WC_i/L$	(Liu <i>et al.</i> , 2015b)
G-GFP	Transfer / output	Linear / non-linear / saturated	No assumption	No assumption	$\mu_{GFP} = \frac{1}{WC_i} \frac{\partial I_D}{\partial [(V_G - V_{th} - V_x) E_x]}$	(Liu <i>et al.</i> , 2019)

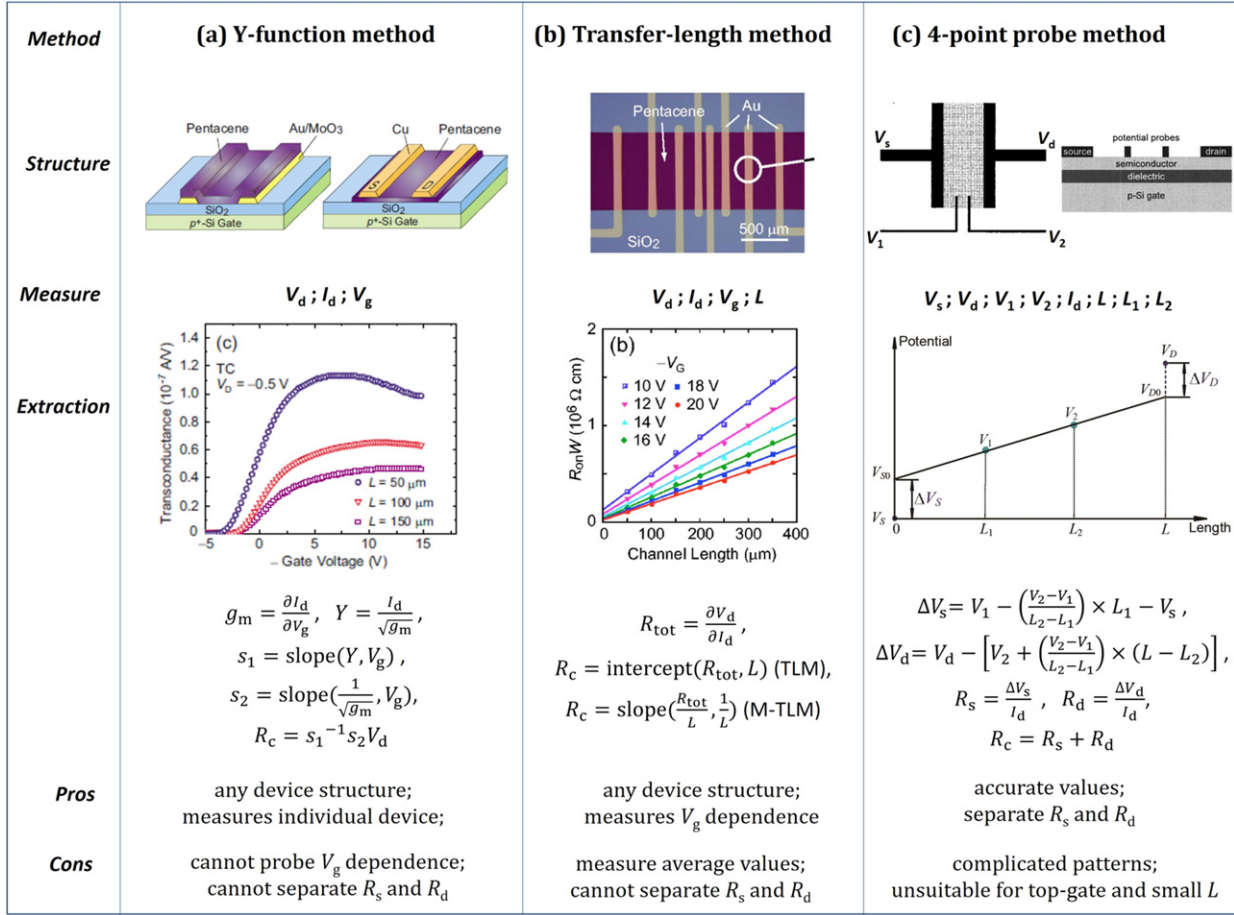


Fig. 16 Representative methods for evaluating contact resistance in OFETs: (a) Y-function method, (b) transfer-line method (TLM), and (c) gated four-point probe method (GFP). Adapted with permission from Liu, C., *et al.*, 2015a. Contact engineering in organic field-effect transistors. Mater. Today 18, 79–96.

violated (Liu *et al.*, 2017b; Rolin *et al.*, 2017; Uemura *et al.*, 2016). The depletion region near the interface or in bulk would reduce the voltage gradient in the channel and thus reduce carrier accumulation (Liu *et al.*, 2017b). Extracting mobility by linear extrapolation using the conventional FET equations (Table 1, FET method) may face errors in selecting the fitting segments and cause concerns about the reliability of mobility (Choi, 2017; Paterson *et al.*, 2018).

To reveal intrinsic transport properties, different measurement methods have been developed and listed in Table 2. The contact effect could be excluded to some extent by the transfer length method (TLM) tests, Y-function method (YFM), or G-function methods (GFM). Some representative methods of measuring contact resistance R_c are illustrated in Fig. 16. The former two are suitable for the linear regime in transfer scanning and the last is for the linear and non-linear regime in output scanning. Alternatively, measuring voltage and current using different terminals, i.e. using gated four point-probe (GFP) or moving probe in scanning Kelvin probe measurement. The experiments identify the voltage drop in the channel and estimate the carrier concentration n . The generalized GFP can be used for arbitrary regimes in FETs (Liu *et al.*, 2019). In addition, Hall-effect in gated devices by magnetic interaction. The carrier concentration n_H only includes the mobile carriers because it is evaluated by the Hall voltage, which results from the balance between the magnetic-field induced current (i.e., Lorentz movement of carriers) and the reversed drift current. These methods have been proven to induce fewer errors in evaluating carrier numbers and mobility (Lee *et al.*, 2013; Rolin *et al.*, 2017).

Notes: (1) TLM: R_{ON} is the transistor on-resistance, expressed as the sum of the channel resistance R_{ch} and the contact resistance R_c as $R_{\text{ON}}(L) = \partial V_D / \partial I_D = R_{\text{ch}}(L) + R_c$. (2) Y-function: g_m is the transconductance. (3) Hall Effect: L^* is the separation between the voltage probes 1 and 2 in the 4-probe conductance measurements. The Hall voltage U_H is determined by subtracting the B independent offset from $V_H(t)$: $U_H(B) = [V_H(B) - V_H(-B)]/2$, and V is the voltage between the two voltage probes. (4) G-function: G is the output conductance. (5) G-GFP: V_x and E_x are the local potential and drift field at the middle point of the two voltage probes, where $V_x = (V_1 + V_2)/2$ and $E_x = (V_1 - V_2)/L^*$. The value of V_{th} can be ready by the threshold of E_x curves.

Showing Carrier Mobility

Presenting carrier mobility of OFETs with a single number allows comparisons feasible but does not reflect the peculiarities in transport properties and device characteristics. When investigating a single value of μ , it should be clearly defined in different scenarios mentioned in Fig. 1 and Table 1. If it is experimentally measured, it should be accompanied by the value of the reliability factor (Choi *et al.*, 2017):

$$r = \begin{cases} \left(\frac{\sqrt{|I_{SD}|^{\max}} - \sqrt{|I_{SD}|^0}}{|V_G|^{\max}} \right)^2 / \left(\frac{|V_{SD}|WC_i}{L} \mu_{lin} \right), & \text{for linear regime} \\ \left(\frac{|I_{SD}|^{\max} - |I_{SD}|^0}{|V_G|^{\max}} \right) / \left(\frac{\partial \sqrt{|I_{SD}|}}{\partial V_G} \right)^2, & \text{for saturated regime} \end{cases} \quad (28)$$

In particular, it is necessary to present μ - V_G curves that would reveal the dominant factors in the bulk or/and at the interfaces and could be referenced to the several possible cases to identify the properties of the transistors and give the information of the whole measurement window and operation of devices (Liu *et al.*, 2017b). Therefore, “a correct measurement of carrier mobility in organic semiconductors has proven challenging” (McCulloch *et al.*, 2016). Also, according to the IEEE test standard, (IEEE, 2008) the μ - V_G dependence should be plotted together with the drain current. An example of the summary is shown in Fig. 17 and Table 3.

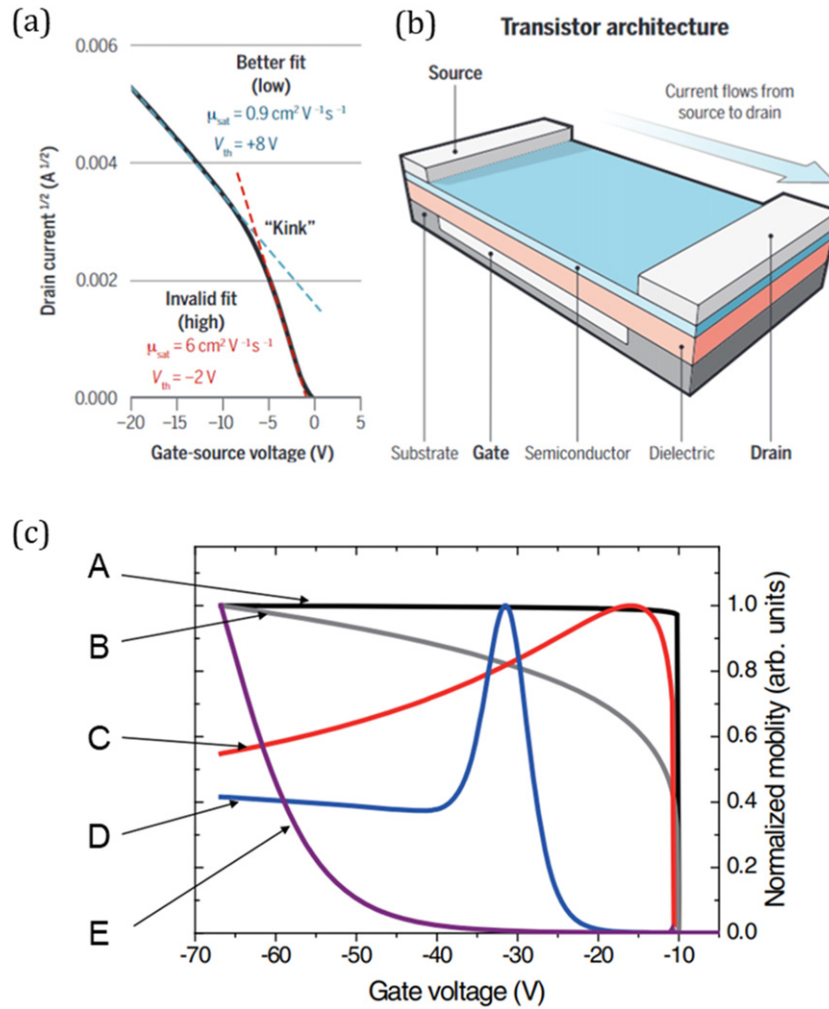


Fig. 17 Non-ideal mobility in OFETs. (a) An example of non-ideal transfer characteristics of a rubrene small-molecule semiconductor device. The difference in the extracted apparent mobility of the two regions of the plot is shown as red and blue extrapolations. (b) Mobility curves of nonideal FETs or TFTs and details are given in Table 3. The values for each curve are normalized to the maximum of each. Adapted with permission from Bittle, *e.g.*, *et al.*, 2016. Mobility overestimation due to gated contacts in organic field-effect transistors. *Nat. Commun.* 7, (10908). Liu, C., *et al.*, 2017b. Device physics of contact issues for the overestimation and underestimation of carrier mobility in field-effect transistors. *Phys. Rev. Appl.* 8, 034020.

Table 3 Mobility curve features in transfer characteristics (above threshold) OFETs

Features (Symbol in Fig. 17) Meanings and possible causes

Constant (A)	Constant mobility with disorder-free charge transport
Power-law increase (B)	Charge transport with localized states near the conduction levels or the band edge (in exponential or Gaussian distribution)
Gradual decay (C)	With resistive contact or surface/phonon scattering of carriers
Sharp peak (D)	With gated Schottky contacts, and the device transits from the Schottky barrier transistor mode to the normal transistor mode
Exponential increase (E)	With gated Schottky contact, and the device works in the Schottky barrier transistor mode

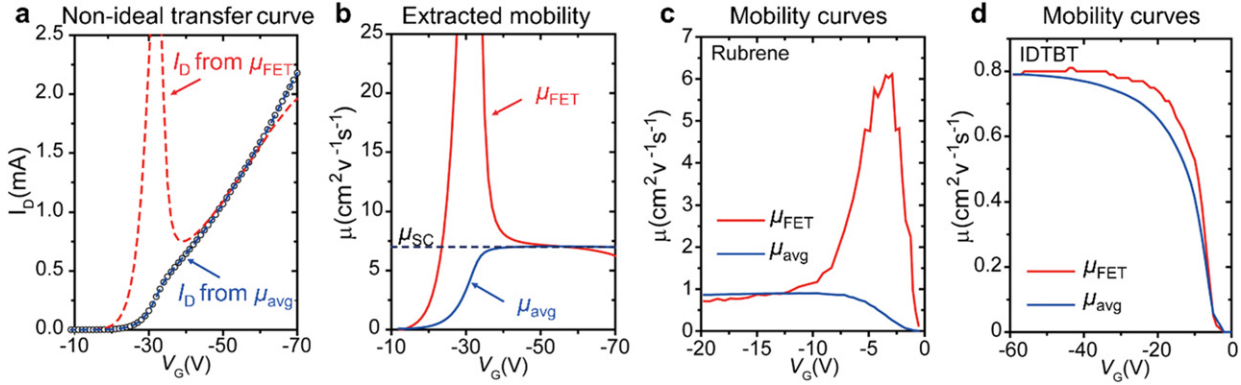


Fig. 18 Mobility presentation. (a) The simulated transfer curve is plotted in hollow circle. For comparison, I_D calculated from Eq. (2) using differential mobility μ_{FET} (linear) and average mobility μ_{avg} (extracted from Eq. 4) are plotted in red and blue lines, respectively. (b) The μ_{FET} - V_G curves and μ_{avg} - V_G curves are compared with the real mobility of the semiconductor. (c-d) The μ_{FET} - V_G curves and μ_{avg} - V_G curves of experimental OFETs with: (c) Small molecule rubrene ($V_D = -20$ V); (d) Polymer IDTBT ($V_D = -60$ V) (the data are taken from literatures). The latter device is closer to ideal OFETs in comparison with the former device. Adapted with permission from Bittle, e.g., *et al.*, 2016. Mobility overestimation due to gated contacts in organic field-effect transistors. *Nat. Commun.* 7, (10908). Deepak, V., *et al.*, 2014. Approaching disorder-free transport in high-mobility conjugated polymers. *Nature* 515, 384–388. Tengzhou, Y., *et al.*, 2019. Understanding, optimizing and utilizing nonideal transistors based on organic or organic hybrid semiconductors. *Adv. Funct. Mater.* 30, 1903889.

Table 4 Factors leading to errors in mobility extraction for OFETs embedded in the parameters of current-voltage relations $I_{lin} = \frac{W}{L} \mu_{lin} C_i (V_G - V_{th}) V_D$ and $I_{sat} = \frac{W}{2L} \mu_{sat} C_i (V_G - V_{th})^2$

Parameters	Factors leading to errors
Channel width W	Fringe current leads to underestimated W
Channel length L	Non-uniform doping leads to overestimated L
Dielectric capacitance C_i	Ions or electric double-layer leads to underestimated C_i
Drain-to-source voltage V_D	Contact potential leads to decreased V_D
Threshold voltage V_{th}	Non-linear injection due to contact problem or transient trapping leads to non-constant V_{th}

Besides, learning from the definition of “average mobility” proposed by Hoffman (2004) one may also sketch the average mobility curves to assess the current-driving properties of transistors, as defined by the slope between each current level at any V_G and that at the threshold point:

$$\mu_{avg}(V_G) = \begin{cases} \frac{L}{WC_i V_D} \left(\frac{I_D}{V_G - V_{th}} \right), & \text{for linear regime} \\ \frac{2L}{WC_i V_D} \left(\frac{\sqrt{I_D}}{V_G - V_{th}} \right)^2, & \text{for saturated regime} \end{cases} \quad (29)$$

An example using simulated Schottky-contact OFETs (the same with (Liu *et al.*, 2017b)) is shown as current and mobility values (Fig. 18(a,b)), where the μ_{avg} curve avoids error brought by fluctuations in local slope that may be caused by non-ohmic contact and noises during scanning. Also, I_D at any V_G can be directly calculated by using μ_{avg} in Eq. (29), as shown in Fig. 18(a). In comparison, if using differential mobility, incorrect I_D would be obtained. Hence, μ_{avg} directly reflects the capability of a transistor in providing current. Fig. 18(c-d) compares the differential and average mobility curves for some OFETs in literature, i.e.,

with small molecule rubrene (Bittle *et al.*, 2016) or with polymer ICTBT (Deepak *et al.*, 2014). The latter device approaches ideal OFETs as the two curves are very close to each other, whereas the former device exhibits obvious non-ideal characteristics due to contact issues.

Overestimating and Underestimating Mobility

According to Eq. (22), errors could be induced by the unexpected non-ideal effects, which include distortion of local potential $V(x)$, dynamic dielectric capacitance C_i due to mobile ions within the dielectric layer, changeable threshold voltage V_{th} due to non-linear charge injection or transient trapping, shortened channel length L due to contact metal diffusion, increased channel width W due to fringe current floating out of the defined channel, decreased drain-to-source voltage drop V_D due to contact potentials, etc. The main factors leading to errors in mobility extraction for OFETs embedded in these parameters are summarized in Table 4.

The material issues that would lead to increased or decreased $V(x)$ and its derivative E_x may come from the electrode-semiconductor interface: (Lamport *et al.*, 2018; Natali *et al.*, 2012) work-function misalignment at the contact, (Rolin *et al.*, 2017; Lindell *et al.*, 2013) interfacial states, (Greiner *et al.*, 2012) semiconductor destruction, (Liu *et al.*, 2018a) injection of minority carriers, (Hu *et al.*, 2016) anisotropic transport, (Li *et al.*, 2018) interfacial trapping near the contact, (Khim *et al.*, 2018) etc. Alternatively, the factors come from near semiconductor-dielectric interfaces: positive or negative fixed charges, transient trapping states, mobile ions, etc. The modifications in potential $V(x)$, E_x , and n often simultaneously occur and they result in various forms of the usually observed μ - V_G relations, (Bouhassoune *et al.*, 2009) which should ideally approach a constant value at various V_G (Deepak *et al.*, 2014). In addition, with small E_x , the mobility could be dependent on E_x for the Poole-Frenkel effect (Arkhipov *et al.*, 2005; Yuki *et al.*, 2008).

The capacitance per unit area for the insulating layer C_i should be ideally independent of measurement frequency, scanning speed, testing history, applied voltage (vertical field), etc. But C_i could be highly dependent on the above testing conditions if using ion gels or electrolytes with a large number of mobile ions, (Cho *et al.*, 2008; Panzer *et al.*, 2008) low-temperature processed or solution-fabricated metal oxide insulators with abundant pinholes or mobile ions, (Sun *et al.*, 2010) or ferroelectric materials with tunable polarizations (Nguyen *et al.*, 2007). Such materials may lead to significantly increased C_i measured at tens to hundreds of Hz as compared with that measured at high frequencies.

For the geometrical parameters in channel width W and channel length L , the fringe current and effectively increased/decreased channel length would affect the value of W/L . The fringe current occurs when the actual channel width can be larger than the apparent width of electrodes. As the fringe current is determined by the lateral electric field and the geometry of electrodes, if the semiconductors are not easily patterned, large W/L (ideally larger than 10 for T-shape channels) should be made to minimize the

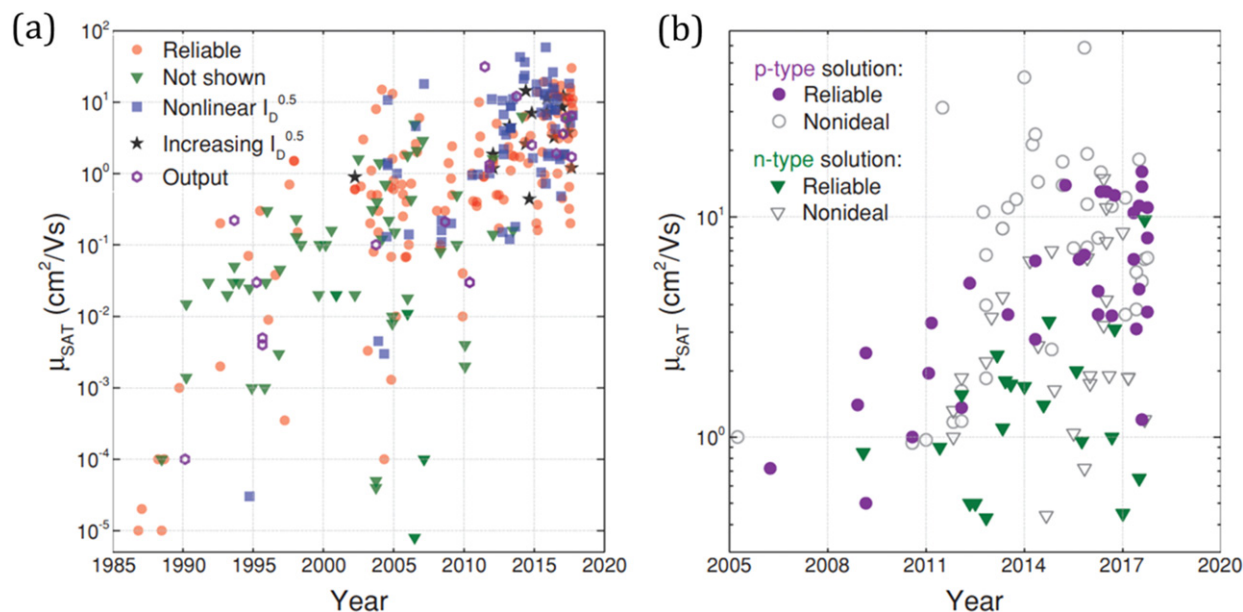


Fig. 19 Mobility values in OFETs. (a) Examination of whether features in the experimental data comply with the classical FET model: reliable (from the data sets shown, there are no obvious nonidealities), not shown (do not show the plot of μ vs V_G or $\sqrt{I_D}$ vs V_G), nonlinear $\sqrt{I_D}$ (the kink or any s-shaped or nonlinear features in $\sqrt{I_D}$ vs V_G), increasing $\sqrt{I_D}$ (the gradient of $\sqrt{I_D}$ gets steeper with V_G), and output (non-saturated output characteristics). (b) Solution-processed data with mobilities approaching $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, by carrier type and data quality, suggesting that 55% of this data set either does not show the data that the mobility was extracted from, or has some sort of non-ideality. Adapted with permission from Paterson, A.F., Singh S., Fallon K.J., *et al.*, 2018. Recent progress in high-mobility organic transistors: A reality check. *Adv. Mater.* 30 (36), 1801079.

effect of fringe current. Errors in channel L come from electrode patterning the electrode in photolithography or shadow-mask evaporation or contact doping and selective doping or using hybridized materials in the channel (negative ΔL) (Blakesley *et al.*, 2014; Hsiao-Wen *et al.*, 2012, 2011; Liu *et al.*, 2012). Small errors could also be induced in short channel OFETs by current crowding effect in the staggering configuration, which extends the effective channel length under the contact-gate overlapping area (Natali *et al.*, 2012; Liu *et al.*, 2014) (usually $< 1 \mu\text{m}$), and drain-depletion region in the saturated regime (usually $< 1 \mu\text{m}$).

Correct estimation of carrier mobility is not only important to evaluate the charge transport mechanisms to guide chemical design and synthesis, but also critical for estimating the organic devices in functional circuits. For example, a transistor with AC applied voltage has a cut-off frequency f_T , beyond which the I_G would finally meet I_D and no amplification could be achieved. Ideal transistors have $f_T = \frac{\mu_{\text{lin}} V_D}{2\pi L^2}$ or $f_T = \frac{\mu_{\text{sat}}(V_G - V_{\text{th}})}{2\pi L^2}$ for the linear regime or saturated regime, respectively. Therefore, maintaining ideal transistor performance, especially high field-effect mobility, in shortchannel devices is critical to obtain a high cut-off frequency. For example, an ideal transistor with the saturated mobility of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $L = 1 \mu\text{m}$, the cutoff frequency at $(V_G - V_{\text{th}})$ of 10 V would reach 1.6 GHz. However, in practical OFETs, semiconductor mobility is no longer limiting the f_T but the contact resistance R_C is the determinant factor, as discussed by Klauk (2018).

Overall, although most studies have still used the FET equations in Table 1 to evaluate transistor performance, non-ideal factors for OFETs or OTFTs are embedded in each above assumption and each parameter contained in Eq. (22), all of which should be optimized to enhance device performance and to guarantee the accuracy of mobility measurements.

Mobility Values

Mobility values measured from organic transistors have been reviewed comprehensively in recent literature from different aspects including synthesis and processing (Wang *et al.*, 2018b; Sun *et al.*, 2019; Wang *et al.*, 2020; Wu *et al.*, 2021; Jiang *et al.*, 2022). Readers may refer to these reviews for mobility values of specific organic compounds or obtain an overview. As benchmarks, organic semiconductors in single-crystal states exhibit higher mobility as compared with polycrystalline or amorphous states (Wang *et al.*, 2018b). Over $40 \text{ cm}^2/\text{Vs}$ and $10 \text{ cm}^2/\text{Vs}$ have been reached respectively in p -type and n -type organic transistors, e.g., with p -type pentacene (Ji *et al.*, 2017) and C8-BTBT (Minemawari *et al.*, 2011) molecules and n -type benzodifurandione-based oligo(p -phenylenevinylene) (BDOPV) (Dou *et al.*, 2015) and tetrachloro derivative (4Cl-TAP) (Chu *et al.*, 2018) molecules.

Despite the large progress, it is notable that high mobility values are sometimes accompanied with non-ideal transistor characteristics as discussed in the previous sections. The mobility values with the ideality have been reviewed with a thorough check by Paterson and Anthopoulos *et al.* (Paterson *et al.*, 2018) and the statistical data are shown in Fig. 19. Therefore, more optimizations are needed to improve the reliability of mobility considering each factor list in Table 4, especially lowering contact resistance (Lamport *et al.*, 2018; Waldrip *et al.*, 2020) and enhancing stability (Okamoto *et al.*, 2020; Iqbal *et al.*, 2021), so that the high mobility can benefit high-frequency MHz circuits (Yamamura *et al.*, 2018; Borchert *et al.*, 2020; Yan *et al.*, 2022), flexible displays (Zhao *et al.*, 2022), sensing and photo-detectors (Wang *et al.*, 2020; Liu *et al.*, 2021b), and emerging memory (Zhu *et al.*, 2020), synaptic (Shao *et al.*, 2021) or biomimetics applications (Shi *et al.*, 2020).

Conclusions

Charge transport in organic semiconductors has been treated by band-like model and hopping model in the simplest approximation, and explored much deeper and more precisely with well-established theories. In general, as proposed by Martin Pope, the band-like transport is suitable for carrier mobility higher than $1 \text{ cm}^2/\text{Vs}$, whereas hopping transport with localized band-tails is considered for carrier mobility lower than $1 \text{ cm}^2/\text{Vs}$. In detail, the quantitative theories cover from microscopic scenarios such as hopping rates, transient localization, or time evolution of the charge wavefunction (Giannini *et al.*, 2019), to macroscopic and statistical distribution of band energy dispersion and dynamic disorders. From experiments, we see VRH model has been used for small molecular or polymer OFETs with mobility lower than $1 \text{ cm}^2/\text{Vs}$, while polaron hopping, nuclear tunneling or transient localization theory gives an explanation for a broader range of organic semiconductors. Importantly, the latter theories can give explicit guiding rules to design organic semiconductors. According to the above theories, the mobility of organic semiconductors could be enhanced via optimizing the molecular design for single crystals, morphological control with uniform sizes of grains or domains for polycrystals, less twisted and more planar backbone for conjugated polymers, etc. Given the rapidly raising speed ever gained (Wang *et al.*, 2018b; Zhang *et al.*, 2018; Guo *et al.*, 2020), we may expect in several years to obtain carrier mobility reliably over $40 \text{ cm}^2/\text{Vs}$ or even approaching $50 \text{ cm}^2/\text{Vs}$ as a milestone of a breakthrough in the understanding of transport in organic semiconductors and to utilize organic transistors practically in various applications (Liu *et al.*, 2018b).

It is also emphasized in this chapter that proper extraction of carrier mobility in electronic devices is critical. As commented by Iain McCulloch *et al.*, "Accurate mobility values are needed by synthetic chemists to validate molecular design concepts aimed at improving charge transport and by circuit designers to ensure that devices can perform their functions." (McCulloch *et al.*, 2016) Measuring and presenting mobility in a careful and accurate way, however clarifying all the measurement conditions and understanding the limitations of the meaning of mobility, is the necessary premise to understand carrier transport to (or not limited to) organic semiconductors.

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Doping in Organic Semiconductors

Yong Xu, Huabin Sun, and Zhihao Yu, College of Integrated Circuit Science and Engineering, Nanjing University of Posts and Telecommunications, Nanjing, China and Guangdong Greater Bay Area Institute of Integrated Circuit and System, Guangzhou, China

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Abstract

A chapter addressing the doping in organic semiconductors is presented. The doping basics is explained in comparison with the conventional inorganic doping for silicon, where the distinct differences provide many insights into the mechanisms behind. Keeping the obtained fundamental understanding in mind, the dopants and the relevant doping techniques are discussed. Finally, the applications of doping to organic devices, mainly about the doping roles in making ohmic contacts and P-N junctions as well as in ameliorating charge transport, are elucidated in details. This is a concise, useful reference for the readers to comprehend doping in organic electronics.

Key Points

- The unconventional doping mechanism, in which the differences with the classical Si doping are elucidated.
- The diverse dopants, in which the presentative and the selection principle are inspected.
- The typical doping techniques, in which the process flow and their applicability are examined.
- The main application to organic electronics, in which the role in making ohmic contacts and P-N junction and in improving the charge transport are discussed.

Introduction

Doping is undoubtedly a key enabler of modern solid-state electronics. It enables the formation of ohmic contacts and P-N junctions that hold the central components of electron devices to realize the designed electrical characteristics. Also, doping has achieved great success in many other aspects. For example, in the current mainstream CMOS technology used for integrated circuit manufacturing, doping is applied to adjust the threshold voltage, to reduce the parasitic effects like the short-channel effects, and the most widely known, to increase the conductivity for lower access resistance (Nishi and Doering, 2000). In a word, doping makes high device performance, low power consumption, and small integrating footprint possible.

Note that, such achievements are all based on the established knowledge and manufacturing technologies (e.g., ion implantation) developed for inorganic semiconductors. As regards the counterpart of organic semiconductors, by contrast, doping is still in the early stage of practical application (Walzer *et al.*, 2007; Lussem *et al.*, 2016; Xu *et al.*, 2018). In particular, the fundamental understanding of doping mechanism remains ambiguous (Jacobs and Moule, 2017; Yoo and Kim, 2015; Salzmänn and Heimel, 2015). As a result, the doping techniques involved in organic device fabrications are simple, e.g., blending, with poor controllability and accuracy. This has severely obstructed the application of doping for organic electronics. In this chapter, we deal with doping in organic semiconductors and address the related main issues. We commence from the doping basics with the classical example of silicon. Then, the doping in organic semiconductors is discussed in comparison with silicon doping. Afterward, we examine the dopants for organic semiconductors and the doping techniques. In the sixth section, the application of doping to organic devices is briefly reviewed.

Doping Basics

For better understanding, we start from inorganic doping with an exemplary semiconductor of silicon (Si). If a single-crystal silicon is undoped (i.e., intrinsic), each Si atom is linked with four neighboring Si atoms by strong covalent bonds; see Fig. 1(a). Its energy band diagram is often simplified as shown in the lower panel, where the Fermi level situates at the midgap, meaning that the concentrations of electron and hole are exactly the same. When dopants (e.g., group V or III elements) are added, they substitute Si atoms after lattice relaxation releasing extra electrons or holes that are free to move in the Si lattice; see Fig. 1(b and c). The silicon becomes extrinsic, that is, the concentrations of electron and hole are no longer identical. Rather, majority carriers and thus minority carriers are produced. If the dopants are group V elements, e.g., phosphorus (P), the majority carriers are electrons and the Si is n-doped. Likewise, if the dopants are group III elements, e.g., boron (B), the majority carriers are holes and the Si is p-doped. From the perspective of the energy band diagram, the dopants create donor/acceptor states below/above the conduction/valence band with a small energy distance apart from the conduction/valence band minimum/maximum, which is the ionization energy (cf. Fig. 1(b and c), lower panel) and generally is small for inorganic dopants, e.g., 45 meV for P and 45 meV for B in silicon (Sze, 1981). Considering the thermal energy of 26 meV at room temperature, those small ionization energies indicate that the dopants can be almost fully ionized under normal operating conditions,

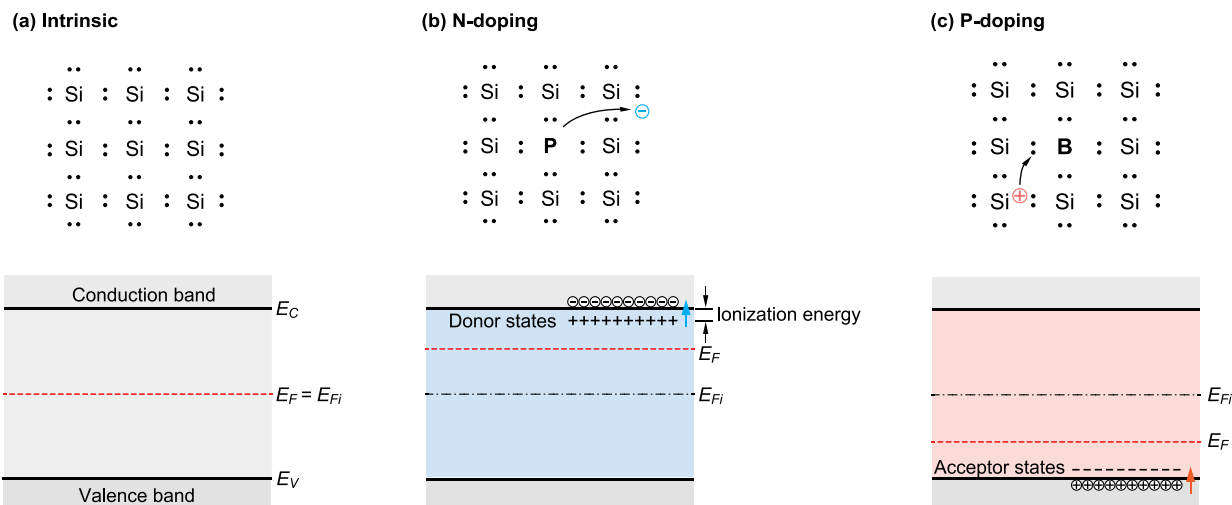


Fig. 1 Illustration of Si doping for intrinsic (a), n-doping (b), and p-doping (c). The upper panels show their bond models, and the lower panels show their energy band diagram.

providing extra, free carriers to participate in the charge transport in electron devices. Accordingly, the Fermi level shifts from the midgap toward the conduction band or the valence band, with more shift at higher doping densities.

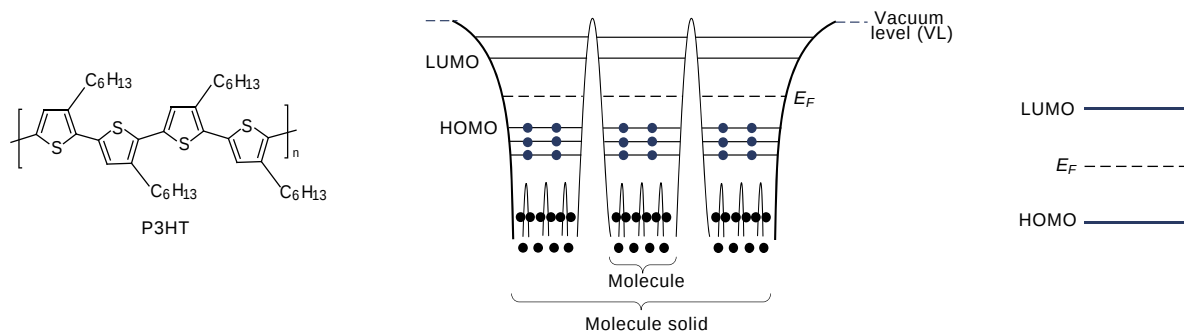
Doping in Organic Semiconductors

In organic semiconductors, the basic unities, molecules, interact each other by weak van der Waals force. This huge difference from Si causes the conduction band and the valence band to disappear (Ishii *et al.*, 1999). Often, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) are employed to represent the conduction band minimum and the valence band maximum, respectively, as depicted in Fig. 2(a). In the absence of dopant, the organic semiconductor (OSC) remains intrinsic and the Fermi level locates at the midgap. After dopants introduced, they present as impurities in the OSC first. Yet, very differently, the dopants cannot substitute the atoms of the host OSC's molecules by forming the covalent bonds, whatever the subsequent processes subjected to. Rather, they still exist in a form of interstitial impurities and electrically interact with the OSC molecules by charge exchange. In short, doping inorganic semiconductors is simply an atomic substitutional process while doping OSC is essentially a molecular interstitial process. Therefore, dopants for OSCs are sometimes called molecular dopants.

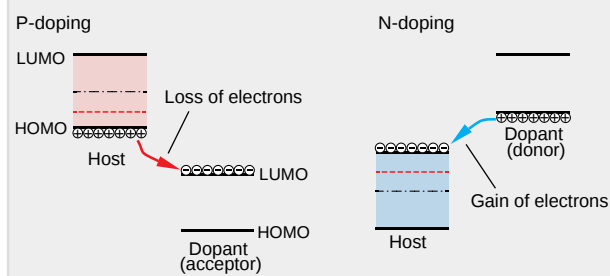
Owing to the charge exchange between dopant and OSC, doping in OSCs is often referred to as charge transfer doping. In order for charge transfer to occur, a high enough energy difference is needed to allow charges to naturally transfer by thermodynamics. As a result of relatively high bandgap of OSCs, e.g., 1.85 eV for small-molecule pentacene and 2.4 eV for polymer poly(3-hexylthiophene) (P3HT), the valence electrons are essentially all distributed in the HOMO under typical circumstances and very few could be thermally activated into the LUMO to become transportable electrons. It connotes that, electrons can be only supplied from the HOMO and just be acceptable by the LUMO. Therefore, for n-doping, the dopant's HOMO should be higher than the OSC's LUMO so that electrons can be transferred from dopant to OSC, i.e., OSC gains electrons and accordingly its Fermi level moves toward the LUMO. Likewise, for p-doping, the dopant's LUMO should be deeper than the OSC's HOMO so that electrons can be transferred from OSC to dopant, i.e., OSC loses electrons and its Fermi level moves toward the HOMO; see Fig. 2(b). Yim *et al.* examined a series of polymeric semiconductors having diverse HOMO levels and blended them with the p-dopant of tetrafluoro-tetracyano-quinodimethane (F_4 -TCNQ) whose LUMO is -5.2 eV. It was found that the doping efficiency indeed depended on the energy offset: with higher conductivity for the larger energy offset, in which P3HT exhibited the greatest doping efficiency for its highest HOMO of -4.8 eV (Yim *et al.*, 2008). Note that, those dopants are supposed to be organics and hence LUMO and HOMO apply instead of the electron affinity and the ionization energy for inorganics.

The suitable, high enough energy offset allows for doping by means of spontaneous charge transfer, where the doping efficiency is regarded as unity, viz., each dopant induces integral charge carriers. This doping is sometimes called *integral* charge transfer with formation of ion pair. However, in some cases, the energy offset is not so high or even negative, but the doping effect is still observable. In the same work of Yim *et al.*, the polymer semiconductors of poly(9,9-di-n-octylfluorene-alt-(1,4-phenylene-(4-sec-butylphenyl) imino)-1,4-phenylene) (TFB) and poly(9,9-di-n-octylfluorenealt-benzothiadiazole) (F8BT) have the HOMO levels of -5.3 eV and -5.9 eV, respectively, which are deeper than the p-dopant's LUMO (-5.2 eV for F_4 -TCNQ), i.e., the energy offset is negative. Unexpectedly, similar doping characteristics to P3HT were observed too, only showing inferior doping efficiency (Yim *et al.*, 2008). This would be another doping mechanism of *partial* charge transfer with formation of the charge transfer complex. The hybridization of the frontier molecular orbitals of the closed dopant and OSC incurs orbital splitting with overlying orbitals unoccupied and underlying orbitals occupied, which serve as an intermediate electron acceptor or donor in place of dopant; as illustrated in Fig. 2(c). This makes the energy levels of dopant (HOMO and LUMO) and thus the energy offset seemingly

(a) Intrinsic



(b) Integral charge transfer



(c) Partial charge transfer

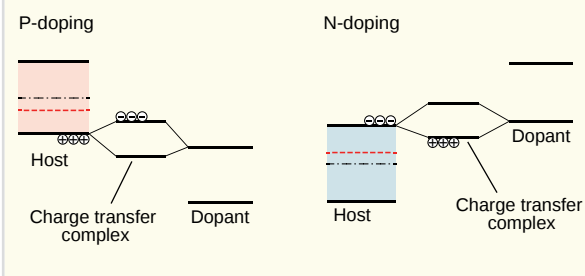


Fig. 2 Illustration of organic doping for intrinsic OSC (a), doping by integral charge transfer (b), and doping by partial charge transfer (c). In (a), the left panel shows the molecular structure of a representative polymer semiconductor of P3HT; the middle panel displays the electronic structure of organic solid; and the right panel illustrates the simplified energy band diagram for OSCs. Reproduced with permission from Xu, Y., Sun, H., Liu, A., *et al.*, 2018. Doping: A key enabler for organic transistors. *Advanced Materials* 30, e1801830. Ishii, H., Sugiyama, K., Ito, E., Seki, K., 1999. Energy level alignment and interfacial electronic structures at organic metal and organic organic interfaces. *Advanced Materials* 11, 605–625. Copyright 1999, 2018, Wiley.

insignificant, yet could lessen the doping efficiency. On the other hand, the orbital splitting has barely been explored to date and is hard to predict and to control. It implies that, the integral and partial charge transfers would be both involved in organic doping. Salzmann *et al.* analyzed the doping in P3HT and quaterthiophene (4T) by using the p-dopant of F₄-TCNQ. They found that the doping process in P3HT was mostly owing to the integral charge transfer while in 4T, the partial charge transfer through the charge transfer complex would be mainly responsible (Salzmann *et al.*, 2016).

Besides energetic consideration, intermolecular geometry in the lately developed donor-acceptor (D-A) copolymers impacts doping too. Using the popular p-dopant of F₄-TCNQ, Nuzzo *et al.* investigated the D-A copolymers of (poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDT-BT) in comparison with the homopolymer of PCPDT (Di Nuzzo *et al.*, 2015). Interestingly, charge transfer arose only if the p-dopant was near the donor (D) unit of CPDT. If the p-dopant was close to the acceptor (A) unit of BT, unfortunately, charge transfer hardly occurred. This selective inactivity of the A units diminished the overall doping efficiency, and was confirmed by the high doping efficiency detected for the homopolymer PCPDT including simply D units of CPDT. Thus, large-molecular-size dopants bridging the D and A units were proposed to overwhelm the limitation in doping the high-performance D-A copolymers.

In addition to charge transfer, alternative explanation for organic doping was proposed, which is the chemical doping. In fact, the charge transfer doping involves re-dox reaction as well. From a chemical point of view, the host OSC losing electrons is oxidized (or p-doped) and the host OSC gaining electrons is reduced (or n-doped), in which the dopants act as oxidizing or reducing agents, respectively. This has been a criterion for selecting the chemical dopants. The representative p-dopant, FeCl₃, is an oxidizing agent widely used to dope small-molecule and polymer OSCs (Chen *et al.*, 2004; Hulea *et al.*, 2005; Xu *et al.*, 2016; Minari *et al.*, 2012). It is noteworthy that introducing small amount of FeCl₃ to OSC (e.g., poly(p-phenylene vinylene) (PPV) and many others) not only increased the OSC's density of states but also improved the carrier delocalization (Hulea *et al.*, 2005; Martens *et al.*, 2003). Other examples of the chemical doping are the acid-based doing by ion transfer and the electrochemical doping by electrolytes. For the former, one can refer to the great article written by Kroon and co-workers (Kroon *et al.*, 2016). For the electrochemical doping, the ultra-thin electric double layers in electrolyte create very large areal capacitance, inducing extremely high charge density to electrically dope the adjacent OSC (Braga *et al.*, 2010). Moreover, the excessive ions diffuse into OSC under strong electrical field to further dope OSC electrochemically. One can refer to ref. (Kim *et al.*, 2013) for more details. So, the chemical doping is electrically similar to the conventional doping (e.g., for Si), no matter what chemical reactions occur and what the products of those reactions are.

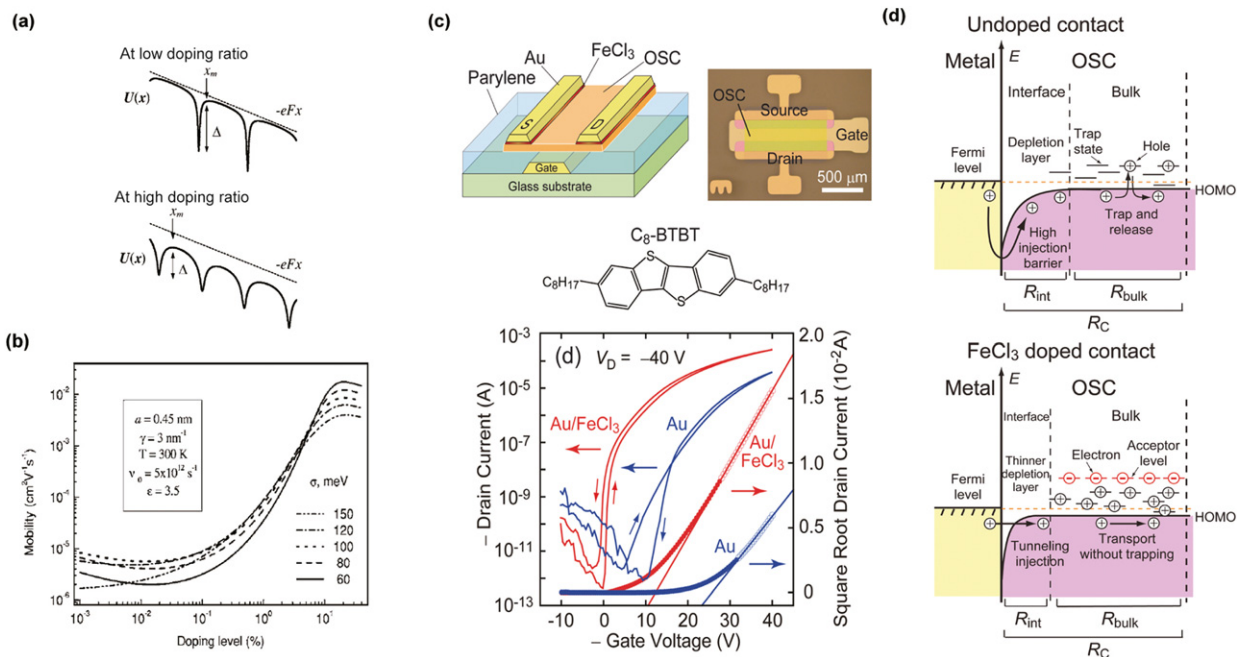


Fig. 3 The influence of doping on the charge transport in organic semiconductors. (a) Impact of the Coulomb traps on the potential landscape at low and high doping ratios. (b) Doping-ratio dependent mobility with the effect of Coulomb traps, where the different line types correspond to the different disorder levels. (c) Device structure of OFETs using the small-molecule dioctylbenzothienobenzothiophene ($\text{C}_8\text{-BTBT}$) with FeCl_3 doped contacts. The right-side figure is an optical image taken on the fabricated device, and the molecular structure of $\text{C}_8\text{-BTBT}$ is also included below. The lower panel shows the typical transfer characteristics measured at a drain voltage of -40 V . (d) Schematic illustration of the charge transport at the contacts before (upper panel) and after (lower panel) contact doping. Reproduced with permission from (a) Arkhipov, V.I., Emelianova, E.V., Heremans, P., Bassler, H., 2005a. Analytic model of carrier mobility in doped disordered organic semiconductors. *Physical Review B* 72, 235202. Copyright 2005, APS. (b) Arkhipov, V.I., Emelianova, E.V., Heremans, P., Bassler, H., 2005b. Effect of doping on the density-of-states distribution and carrier hopping in disordered organic semiconductors. *Physical Review B* 71, 045214. Copyright 2005, APS. (c) Minari, T., Darmawan, P., Liu, C., *et al.*, 2012. Tsukagoshi, Highly enhanced charge injection in thienoacene-based organic field-effect transistors with chemically doped contact. *Applied Physics Letters* 100, 093303. Copyright 2012, AIP.

Finally, let's look at the expression of organic doping in the energy band diagram and briefly discuss the relevant charge transport issues. Since no atomic substitution involved in organic doping, the dopants may not create donor and acceptor states in the OSC's bandgap (that's why the dopant's energy levels are usually drawn next to the OSC instead of the center of the OSC's bandgap), which means that the ionization energy would not be applicable. Nevertheless, one can still estimate it for qualitative understanding. According to the theory of ionization energy defined for hydrogen atom, a donor's ionization energy can be calculated through $(\epsilon_0/\epsilon_s)^2(m_{ce}/m_0)E_H$, where ϵ_0 and ϵ_s are the permittivity of vacuum and semiconductor, respectively; m_{ce} is the effective electron mass in the conduction band (here is the LUMO), m_0 is the electron rest mass, and E_H is the ionization energy of the hydrogen atom ($= 13.6 \text{ eV}$) (Sze, 1981). In general, OSCs have small permittivity, e.g., $\epsilon_s = 3.5$ and 4.4 for small-molecule pentacene and polymer P3HT that are much smaller than $\epsilon_s = 11.9$ for Si. The effective electron mass in OSCs are much greater (e.g., $m_{ce} = 1.7m_0$ in P3HT) compared to that in silicon (a few times lesser than m_0) (Jeon *et al.*, 2001). Hence, the ionization energy for a donor in OSC could be higher than in Si by magnitudes, and likewise for acceptors. Such high ionization energies signify that, in OSCs, the dopants and the induced charge carriers cannot be fully dissociated, but still strongly associated in a fashion of Coulomb pairs or bipolarons (Arkhipov *et al.*, 2005a). The presence of electron-hole pairs builds Coulombic potential wells along the transport pathway, increasing energetic disorder to further deteriorate the profile of charge transport such that the doping-induced charge carriers would be nearly localized at the beginning; see Fig. 3(a). Only at high enough doping ratios, those potential wells overlap and the transport pathway is smoothened, i.e., that energetic disorder fades away. This effect is particularly pronounced for the OSCs of high quality, manifesting itself as a decreasing mobility at first and then turning to increase with doping concentration (cf. Fig. 3(b)) (Arkhipov *et al.*, 2005a,b). Despite that, most OSCs still contain large numbers of defects and disorders and thus the charge transport therein is basically a hopping process (Venkateshvaran *et al.*, 2014). The hopping barrier is lessened by the elevated Fermi level via doping, or the hopping probability is enhanced. As a result, the mobility rises monotonically with doping, particularly fast at low doping ratios where the charge carriers are freed from deep traps, referred to as trap passivation or trap filling (Minari *et al.*, 2012; Tietze *et al.*, 2015; Olthof *et al.*, 2012), as depicted in Fig. 3(c and d). At very high ratios, on the other hand, doping may not be always beneficial. An important reason is that the high-density dopants (in fact being impurities) start to affect the OSC microstructure adversely, and the mobility tends to saturate or decreases with the doping ratio (cf. Fig. 3(b)) (Arkhipov *et al.*, 2005a; Chiang *et al.*, 1977).

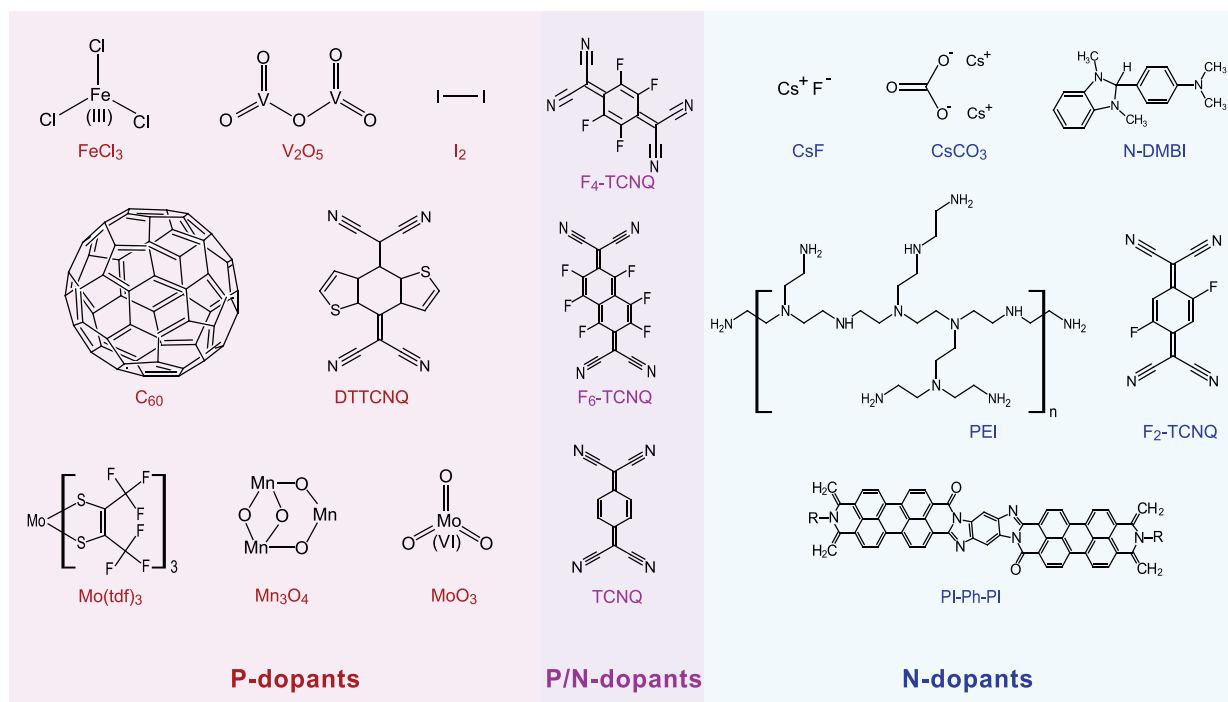


Fig. 4 Molecular structures of the some representative dopants. Reproduced with permission from Xu, Y., Sun, H., Liu, A., *et al.*, 2018. Doping: A key enabler for organic transistors. *Advanced Materials* 30, e1801830. Copyright 2018, Wiley. For the sake of simplicity, the abbreviations of the dopant molecules are provided instead of their full names, please refer to the relevant references for more details.

Dopants for Organic Semiconductors

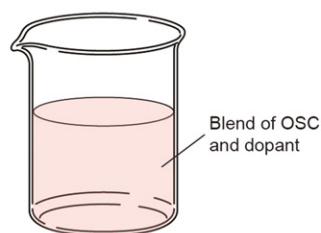
The dissimilar doping mechanisms between inorganic and organic result in quite different dopants and selecting principles. Regarding the inorganic example of Si, group V and III elements are the typical n- and p-dopants, respectively. Those elements, however, seldom apply in their simple form but mostly in a chemical state; e.g., P_2O_5 (solid), POCl_3 (liquid), and PH_3 (gas) are commonly used rather than P, where proper chemical reactions should be premeditated (May and Spanos, 2006). Regarding the OSCs, there have been a wide variety of dopants exploited, including organics, metals, metal oxides, and organic-metallic complexes. Some representative dopants are shown in Fig. 4. If the dopant is *organic*, the selection is simple. According to the charge transfer doping, the n-dopant should have shallow enough HOMO and the p-dopant should have deep enough LUMO. A typical p-dopant is $\text{F}_4\text{-TCNQ}$ for its deep lying LUMO of -5.2 eV that is lower than numerous OSCs' HOMO (Yoo and Kim, 2015; Yim *et al.*, 2008). If the dopant is *metal*, one needs to take its work function into account for the electrons being transferrable from the metal Fermi level to the OSC LUMO. Therefore, the metal dopants are basically n-type, e.g., alkali metals with small work functions like Li and Cs (Kido and Matsumoto, 1998). As alkali metals are highly unstable in air, their compounds like LiF and CsF are more often utilized, also as n-dopants (Khim *et al.*, 2014; Yuan *et al.*, 2004). With regard to *metal oxides* and other agents, their chemical characteristics, namely oxidative (electron-withdrawing) and reductive (electron-donating) properties are considered for the use of p-dopant and n-dopant, respectively. The typical oxidative p-dopants include MoO_3 , V_2O_5 , and FeCl_3 (Xu *et al.*, 2016; Kano *et al.*, 2009; Baeg *et al.*, 2013; Meyer *et al.*, 2011); and the typical reductive n-dopant is polyethylenimine (PEI) (Zhou *et al.*, 2012). For the *organic-metallic complexes*, tris[1,2-bis(trifluoromethyl) ethane-1,2-dithiolene] ($\text{Mo}(\text{tfd})_3$) is often used as a p-dopant (Lee *et al.*, 2011). It should be mentioned here that, the identification of those dopants as p-type or n-type has essentially been based on experimental observations, among which a notable situation is that some of dopants could behave both as p-type and n-type, e.g., $\text{F}_4\text{-TCNQ}$ (Tadaki *et al.*, 2016; Higashino *et al.*, 2016). This would be related to the OSC applied, the formation of the charge transfer complex, as well as the generation of the gap states (Hirose *et al.*, 1996a). And over the doping type, the doping efficiency, stability, accessibility, and processability are important to the dopants for OSCs. For more details about the dopants for OSCs, one can refer to the related references (Xu *et al.*, 2018; Jacobs and Moule, 2017; Yoo and Kim, 2015; Lussem *et al.*, 2013).

Doping Techniques

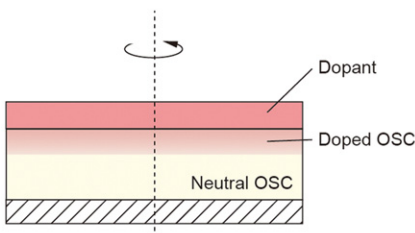
Diffusion and ion implantation are the well-known techniques for Si doping. After dopants introduced, thermal annealing or rapid thermal annealing is applied to repair the damaged lattice and to activate dopants, during which the dopants (e.g., P after reduction) diffuse and substitute the Si atoms to be linked with the surrounding Si atoms by the covalent bonds. These established approaches,

(a) Solution-based processes

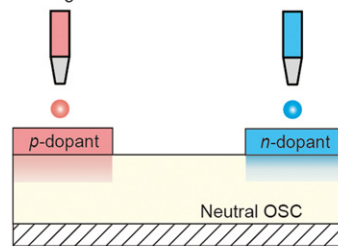
Blending



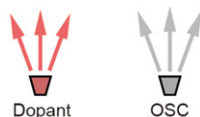
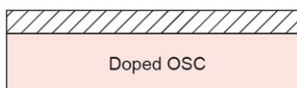
Coating & Dipping over OSC



Printing

**(b) Thermal evaporation**

Co-deposition



Deposition

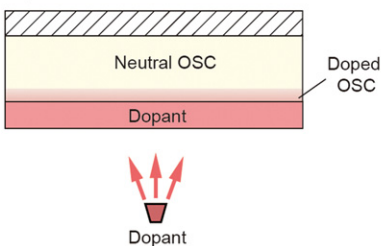
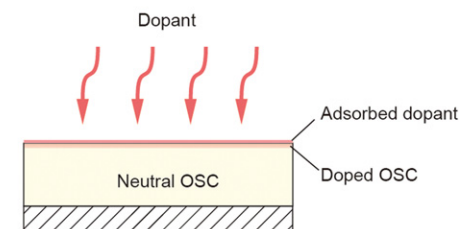
**(c) Physisorption**

Fig. 5 Schematic illustration of the doping techniques for organic semiconductors. (a) Solution-based processes. (b) Thermal evaporation. (c) Physisorption. Reproduced with permission from Xu, Y., Sun, H., Liu, A., *et al.*, 2018. Doping: A key enabler for organic transistors. *Advanced Materials* 30, e1801830. Copyright 2018, Wiley.

however, are not applicable to OSC since the high temperature (e.g., $> 1000^{\circ}\text{C}$) and the high energy (e.g., $\geq 50\text{ keV}$) can destroy the fragile organic layers and even the entire organic devices. Hence, the doping techniques for OSC are, in principle, very gentle.

Solution-based doping is appealing for the potential of providing large area, flexibility, and low cost. *Blending* dopant and OSC in solution is facile to implement, where the doping concentration can be precisely regulated (cf. Fig. 5(a), left panel) (Ma *et al.*, 2008). Yet, the dopant distribution is not manageable since the OSC film is homogeneously doped. This is not suited to circuit fabrications that require complex doping pattern and doping profile. Also, the presence of dopants (actually as impurities) may interrupt the self-organization of OSC molecules during the film formation. The charge transport efficiency would be degraded. For this reason, high doping ratio should be reservedly used. *Coating* (spin coating, spray coating, bar coating etc.) of dopant solution over the OSC film or vice versa are popular for organic doping (cf. Fig. 5(a), middle panel) (Long *et al.*, 2014). Compared to blending, the doping process here is separated from the manufacture of the OSC film so that high-quality OSC film can be separately prepared. Moreover, the doping distribution in depth can be regulated by controlling the diffusion (e.g., the dopant's diffusivity and the subsequent annealing) (Kolesov *et al.*, 2017), similar to the diffusion in doping Si. Nevertheless, the lateral distribution remains uncontrolled. Furthermore, finding solvents simultaneously suited to the dopant and the adjacent organic layer is not easy. For the former, high solubility is requisite, but for the latter, insolubility or orthogonality is imperative. This may additionally degrade the performance of the organic devices fabricated via successive layer-by-layer depositions. *Dipping* the OSC film into the dopant solution is analogous to coating, with the difference that the OSC surfaces are fully doped. *Printing* (inkjet printing, screen printing etc.), on the other hand, is quite suitable for circuit fabrication, by which doping is localized in small areas and different types of dopants (p and n) can be selectively applied for individual devices (cf. Fig. 5(a), right panel), important to the complementary integrated circuit (IC) (Khim *et al.*, 2014). They together eliminate the utilization of patterning process, e.g., lithography. It is known that photolithography shares the major cost of the present IC manufacturing. Therefore, printing in particular roll-to-roll printing is promising for the future flexible organics.

Thermal evaporation is another popular doping technique, mostly for small-molecule OSCs, which are often insoluble in organic solvents. The doping process is similar to solution-based doping discussed above, but is in solid state here. *Co-deposition* of dopant and OSC together is a solid-state doping method similar to blending (Tietze *et al.*, 2015; Harada *et al.*, 2007), where the doping ratio can be controlled by adjusting their evaporating rates and the adverse effect to the OSC morphology calls for caution too (cf. Fig. 5(b), left panel). *Deposition* of dopant and OSC in sequence is alternative solid-state doping method similar to the doping by coating, where the doping process mainly occurs at the OSC surface next to the dopant layer (cf. Fig. 5(b), right panel) (Lu *et al.*, 2013). The doping dose can be roughly estimated by altering the dopant layer thickness. Since the film formation and doping are all in solid state, shadow masks are commonly used to confine the doping area, e.g., contact doping in organic transistor fabrication (Ante *et al.*, 2011; Tsukagoshi *et al.*, 2007). Also, high-quality OSC film like the highly crystalline small molecules (e.g., pentacene) can be retained for the separated film formation from the doping process.

Physisorption, sometimes called dopant vapor exposure, is a special doping method (cf. Fig. 5(c)). Its specialty stems from a fact that many species in our environment, e.g., oxygen and water, can behave as dopants for OSCs and often cause unintentional doping effects (Lu *et al.*, 2013). The dopants are physically absorbed by the OSC surface and diffuse into the OSC bulk and finally embedded

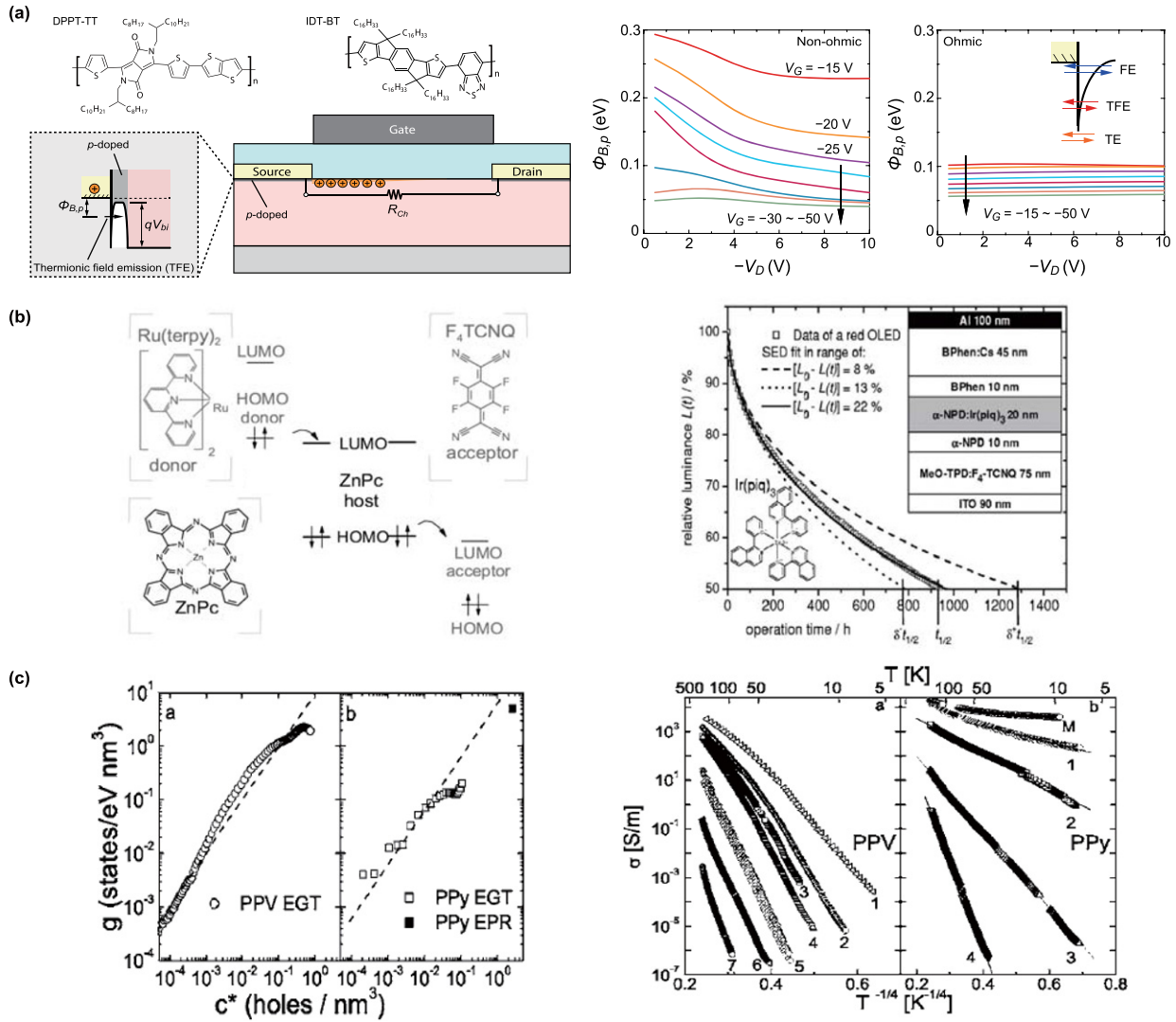


Fig. 6 Application of doping to organic devices. (a) Ohmic contacts in polymer OFETs with FeCl₃-doped contacts. The left panel shows the device structure and the molecular structures of the D-A copolymers, where the charge injection via high-efficient thermionic field emission is highlighted. The right panel shows the Schottky barrier versus the gate voltage. In the case of non-ohmic contact, the Schottky barrier is high and highly gate-voltage dependent, while in the ohmic-contact case, the Schottky barrier is low and gate-voltage independent. (b) P-N junction fabrication and its application. Left panel: OSC (ZnPc) and its n-dopant (donor) and p-dopant (acceptor) to make an organic P-N homojunction. Right panel: ultra-stable and high-efficient red OLEDs achieved with doped transport layer. (c) Improved charge transport. Left panel: the density of states plotted versus the doping level in log-log scale, where a linearly increasing tendency can be observed. Right panel: conductivity plotted with temperature in semi-log scale, where a metallic transition can be spotted for PPy at high doping level. Reproduced with permission from (a) Xu, Y., Sun, H.B., Li, W.W., *et al.*, 2017b. Exploring the charge transport in conjugated polymers. *Advanced Materials* 29, 1702729. Copyright 2017, Wiley. (b) Harada, K., Werner, A.G., Pfeiffer, M., *et al.*, 2005. Organic homojunction diodes with a high built-in potential: Interpretation of the current-voltage characteristics by a generalized Einstein relation. *Physical Review Letters* 94. Copyright 2015 APS. Meerheim, R., Walzer, K., Pfeiffer, M., Leo, K., 2006. Ultrastable and efficient red organic light emitting diodes with doped transport layers. *Applied Physics Letters* 89. Copyright 2006, AIP. (c) Hulea, I.N., Brom, H.B., Mukherjee, A.K., Menon, R., 2005. Doping, density of states, and conductivity in polypyrrole and poly(p-phenylene vinylene). *Physical Review B* 72, 054208. Copyright 2015 APS.

in the OSC matrix. As these species are basically inevitable, the as-fabricated OSC film would be pre-doped, leading to unwanted device characteristics (Nikolka *et al.*, 2017). Thus, the fabrication of organic devices, in particular the OSC film deposition, is usually performed in nitrogen-filled glovebox or in high vacuum chamber. Certainly, other gaseous dopants like ammonia (NH₃) and iodine (I₂) vapor can also dope OSCs by this method (Lee *et al.*, 2016). Yet, one needs to note that physical absorption is very unstable. The absorbed dopants can be almost completely removed by annealing, that is, the OSC is de-doped (Lee *et al.*, 2016). For this reason, together with the high diffusivity of gaseous dopants in OSCs, practical application of this doping technique may be limited.

The doping techniques for OSC are so simple that serious issues may be caused. *Dopant diffusion* is often sizable as dopants are still mobile even after the doping process. This is in contrast to Si doping in which the ionized dopants (e.g., P⁺) are fixed by the strong covalent bonds with the neighboring Si atoms, meaning that P⁺ is unable to diffuse after atomic substitution. Rapid thermal

annealing (e.g., over few seconds) is applied to minimize the dopant (P , not P^+) diffusion before atomic substitution, enabling abrupt and shallow doping profile to be made. This is of great importance to the devices with small feature size. A similar scheme was reported by Tang and co-workers. The counter-ions were also covalently bonded with the polymer OSC backbone by electrically insulating “linker” so that stable doping profile could be achieved (Tang *et al.*, 2016). *Doping instability* is another serious problem. The ambiguous doping mechanism may be one of the reasons, since the charge transfer by thermodynamics is essentially a statistical result. That means, the transferred electrons may return back to their initial states upon heating and irradiation, particularly true for the doping involving the charge transfer complex. And then, the doping effect vanishes. Measures must be taken to prevent this phenomenon from happening. Lin *et al.* reported an interesting approach to circumvent this issue. The dimeric n-dopant of (pentamethylcyclopentadienyl) (1,3,5-trimethylbenzene) ruthenium dimer ($[RuCp^*Mes]_2$) cleaved upon an endergonic process of photo activation, giving rise to stable charge transfer that can beat the thermodynamic limit (Lin *et al.*, 2017). Note that, the highly diffusive and unstable dopants, mainly for n-dopants such as alkali metals, can degrade the doping stability as well. For more details on the doping techniques and the dopants involved, one can refer to the reference (Xu *et al.*, 2018).

Application of Doping to Organic Devices

Doping has played significant roles in multiple organic devices, including organic field-effect transistor (OFET), organic light-emitting diode (OLED), and organic photovoltaic (OPV), mainly for ohmic contacts, P-N junction, and improved charge transport.

Ohmic contacts enable efficient charge injection and extraction, and thus are crucial for all types of organic devices. Ohmic contacts can be achieved by two ways: non-rectifying contacts and tunneling contacts. The former necessitates small Schottky barrier (< 0.15 eV), viz., the metal's Fermi level should well align with the OSC's transporting level (LUMO/HOMO). Accordingly, high-work-function metals are often used for p-type OFET's source/drain electrodes and OLED's or OPV's anode, and low-work-function metals are employed for n-type OFET's source/drain electrodes and OLED's or OPV's cathode (Xu *et al.*, 2017a). However, the metals with low work functions (e.g., Ca) are typically unstable and highly diffusive, making n-type ohmic contacts problematic. This is, obviously, detrimental to OLEDs and OPVs that demand balanced electron-hole injection and extraction, and also explains in part why the development of n-type OFETs is slower than the p-type counterparts. The latter, tunneling contacts, from another perspective, necessitate very thin Schottky barrier such that the charge carriers can pass through via tunneling. Heavily doping OSC raises the carrier concentration up to 10^{20} cm^{-3} , at which the thickness of the space charge layer can be reduced to be as thin as few nanometers, a tunnelable distance under normal conditions (Khim *et al.*, 2014). Then, the height of the Schottky barrier becomes unimportant, or the effective Schottky barrier height is very small; as shown in Fig. 6(a). Substantial improvements in device performance are often observed (Xu *et al.*, 2016, 2017b). Taking OFETs as example, it has been extensively reported that contact doping not only decreased the contact resistance (e.g., $10 \text{ } \Omega \text{ cm}$ for the electrochemically doped P3HT OFETs (Braga *et al.*, 2010)) but also greatly promoted mobility (Singh *et al.*, 2013), the threshold voltage (Minari *et al.*, 2012), and the subthreshold swing (Kano *et al.*, 2009). For OLEDs, their external quantum efficiency and power efficiency were noticeably enhanced by including charge injection layers (Zhou *et al.*, 2012; Tang *et al.*, 2016). Such pronounced improvements reflect a fact that the charge transport in organic devices is, in general, limited by the charge injection/extraction at contacts, and doping can bypass this barrier. It needs to be pointed out that, the presence of dopants at the metal-OSC interface can create gap states and broaden the density of states (Hirosue *et al.*, 1996a,b; Xu *et al.*, 2014; Hosseini *et al.*, 2005), together making non-rectifying ohmic contacts possible. No matter what's the dopant role, the result is the same: the Schottky barrier height becomes insignificant. It, on the other hand, implies that the selection of metal for electrodes is more flexible. This has profound implication in terms of manufacturing and cost control.

P-N junction (in fact its built-in potential) holds the key element in organic devices, especially for the diode-based OLEDs and OPVs. Differently doping OSC shifts the Fermi level toward the HOMO and LUMO respectively. When the p- and n-doped OSCs are brought to making contacts, their Fermi levels align, inducing a built-in potential whose value is equal to the difference in the Fermi level. The higher the doping ratio, the larger the Fermi level shift, and hence the greater the built-in potential. This potential can serve as a charge blocker in field-effect transistors and a charge separator in photovoltaic cells, so its magnitude and electrical properties are vital. Recall that inorganic semiconductors permit successive doping of different types (called compensation). P-N junction can be easily made by beginning with an n-type semiconductor and adding excess p-dopants to the selected area to convert it to be p-type, and vice versa. This great methodology, unfortunately, is not applicable to OSCs for the incompatible doping mechanisms and technologies. As a result, stable, abrupt, and high-quality (low defects) P-N junctions are challenging for organic devices. Instead, P-N junctions or P-i-N junctions using two different OSCs with opposite doping types and an intrinsic layer have been extensively explored (Walzer *et al.*, 2007; Lussem *et al.*, 2013), where an intermediate intrinsic layer is used to guarantee the ideality of the junction properties and hence the most P-N junctions in the literature are P-i-N style. These junctions are referred to as heterojunctions rather than homojunctions based on a single OSC. Up to now, only few demonstrations have succeeded homojunctions using suitable combination of OSC and p/n-dopants to achieve high built-in potential (Harada *et al.*, 2005), as shown in Fig. 6(b), left panel. With regard to the practical OLEDs or OPVs, doping is applied to heterojunctions. For instance, doping the charge transport layers greatly improved the device performance and stability (Meerheim *et al.*, 2006), as shown in Fig. 6(b), right panel. Finally, it should be pointed out that, P-N junctions may not always exist in typical OFETs without doping, so the Schottky barrier and its built-in potential may takeover to block the charges at the source contact front (Xu *et al.*, 2018, 2017b).

Improving charge transport is another benefit of doping. As discussed in Section “Doping in Organic Semiconductors”, the charge transport in OSCs is basically a hopping process involving a large number of defects and disorders. Doping OSC elevates the Fermi

level toward the transporting states, passivating traps in the band gap and alleviating the influence of energetic disorders. Moreover, doping was found to promote the density of states (Hulea *et al.*, 2005), as illustrated in Fig. 6(c), left panel. They combined lead to greatly upgraded carrier delocalization, or mobility. If considering the raised carrier concentration, the conductivity can be considerably increased (cf. Fig. 6(c), right panel) (Hulea *et al.*, 2004), since the conductivity $\sigma = nq\mu$ where n is the carrier concentration, q is the elementary charge, and μ is the mobility. Higher conductivity is wanted for smaller access resistance (for OFETs) and lower voltage drop while crossing the charge transport layers (for OLEDs and OPVs). Aside from superior mobility and conductivity, the improved charge transport can be manifested as better stability and uniformity (in electrical characteristics from device to device) (Khim *et al.*, 2014; Hein *et al.*, 2014; Hu *et al.*, 2012), which is, evidently, of great value for commercial applications.

Outlook

Doping is so important to organic electronics that breakthroughs in performance have mostly been associated with doping's participation. Meanwhile, many challenges still remain unsolved. Above all, the ambiguous doping mechanism calls for illumination. And then, a unified, versatile doping technique can be established to enable high-quality doping profile comparable to inorganic rivals being made, in which the issues on dopant diffusion and instability should be well resolved. After that, even higher performance organic devices and integrated circuits with doped functional layers can be truly envisaged.

Conclusion

The weak interaction of van der Waals force among molecules is the origin of the great flexibility of OSCs, yet it leads to the disappearance of the energy band and very low carrier delocalization rate. The charge transport in OSCs is thus, basically, by hopping involving a great number of defects and disorders. Because of those distinct differences from inorganic semiconductors, doping OSCs is fundamentally different from Si and essentially a molecular interstitial process. The dopants still present as interstitial impurities in the host OSC matrix and only electrically interact with the near OSC molecules by charge transfer. The low doping efficiency and low stability are serious problems. As a result, the doping techniques for OSCs are very simple with poor controllability and accuracy. This is certainly detrimental to the fabrication of electronic devices for practical applications. More researches in particular to illuminate the doping mechanism are urgently needed.

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Single-Crystal Organic Semiconductors

Wenping Hu and Xiaochen Ren, Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Department of Chemistry, School of Science, Tianjin University & Collaborative Innovation Center of Chemical Science and Engineering, Tianjin, China.

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Abstract

Single-crystal organic semiconductor plays an important role to realize high-performance organic electronic devices. It has unique molecular aggregation modes and optoelectronic properties due to the weak van de Waals interaction between organic molecules. Here in, the fundamental knowledge of organic single crystal and their optoelectrical properties, as well as the materials, processing, and devices of single-crystal organic semiconductors are summarized. Finally, the future research directions of this field are suggested.

Nomenclature

C₈-BTBT 2,7-dioctyl[1]benzothieno[3,2-*b*]benzothiophene
C₆-DBTDT dihexyl-substituted dibenzo[*d,d'*]thieno[3,2-*b*;4,5-*b'*]dithiophene
C₆-DNT-VW hexyl-substituted dinaphtho[2,3-*b*:2',3'-*d'*]thiophene
C₁₀-DNTT 2,9-didecyldinaphtho[2,3-*b*:2',3'-*f'*]thieno[3,2-*b*]thiophene
DPA 2,6-diphenyl anthracene
DNTT dinaphtho[2,3-*b*:2',3'-*f'*]thieno[3,2-*b*]thiophene
HOMO highest occupied molecular orbital
NIR near infrared
TFT-CN 2,2'-((5*Z*,5'*Z*)-5,5'-(furan-2,5 diylidene) bis(4-octylthiophene-5,2(5H)-diylidene)) dimalonilile
TiOPc Titanyl phthalocyanine
TIPS-pentacene 6,13-Bis(triisopropylsilyl)ethynyl)pentacene
TIPS-TAP 6,13-bis((triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacene

Key Points

- The molecular aggregation modes and unique optoelectronic properties of single-crystal organic semiconductor are summarized.
- High-performance single crystal materials is reviewed.
- Insight into single crystal OFET and phototransistor device operation is provided.

Introduction

Organic electronic devices are known as the promising candidate for the next generation electronics due to their intrinsic flexibility, low-cost and solution processability. Various types of electronic devices have successfully demonstrated based on organic semiconductors including solar cells, (Cheng *et al.*, 2009; Peumans *et al.*, 2003) organic light emitting diodes (OLEDs), (Li *et al.*, 2013; Liao *et al.*, 2008; Tang and VanSlyke, 1987) transistors, (Chua *et al.*, 2005; Klauk *et al.*, 2007; Mei *et al.*, 2013) thermoelectric junctions, (Sun *et al.*, 2012) and resistive switch memory cells (Scott and Bozano, 2007; Song *et al.*, 2010). In organic semiconductor, the charge transport is mainly dominated by the π -electron overlapping between adjacent molecules, therefore a long-range ordered packing of organic molecules would be critical for fluent charge transportation. Single crystal organic semiconductors fulfill the requirement for high-performance organic devices because of their defect free nature that eliminating grain boundary and impurity, as well as their unique optoelectronic properties such as band-like transport property and long exciton diffusion length. For example, the reliable charge carrier mobility of single crystal organic field-effect transistors (OFETs) has reached over $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, (Paterson *et al.*, 2018) outperforming the amorphous silicon devices. Novel property that combining high mobility and strong electroluminescence together on the same material has been demonstrated for DPA organic single crystals (Liu *et al.*, 2015) therefore enabling novel optoelectronic applications such as organic light-emitting transistors (OLETs) or electrically pumped organic lasers (Li *et al.*, 2017; Zhang *et al.*, 2018). In addition, organic single crystals with only a few or monolayer of molecules show different electrical behavior from their bulk form, leading to superior device performance for various applications including OFETs, phototransistors and sensors (Peng *et al.*, 2020; Wang *et al.*, 2018b).

In this article, we will provide an overview of single crystal organic semiconductors starting from fundamental knowledge of organic single crystal and their optoelectrical properties, followed by the materials, processing, and devices of single crystal organic

semiconductors in the main body. We mainly focus on the materials and operation of OFET device which is the fundamental unit to construct organic integrated circuits. Finally, suggestions of future research direction for this field are provided.

Backgrounds

Organic small molecules or polymers that containing conjugated π -systems could be potentially used for semiconductor applications. In these materials, electrons are delocalized within the π -system (π -molecule orbitals) due to the weak π bond energy, and they have a chance to transport from one molecule to another when the π -molecule orbitals of two neighboring molecules overlap with each other. To practically utilize organic semiconductor for electronic devices, long-range ordered molecular packing is required for continuous charge transport. The understanding of molecular aggregation modes and transport properties is also important for the development of organic electronics. In this section, we briefly introduce these two aspects based on organic small molecular materials for their overall good crystallinity. Some of the conjugated polymers can also form single crystal and their progress are summarized elsewhere (Yao *et al.*, 2017).

Molecular aggregation modes

Unlike silicon crystals that Si atoms are connected by covalent bonds, the aggregation of conjugated small molecules in organic single crystals is governed by weak van de Waals force. This driving force fundamentally leads to the unique molecular aggregation modes, crystal structures as well as optoelectronic characteristics of organic semiconductors. Generally, there are five different modes of molecular aggregation according to their relative position, and thus further induces four different molecular packings in 3D assemblies as illustrated in Fig. 1.

The simplest case is that two molecules are completely in a face-to-face arrangement as shown in Fig. 1(a), which is called ideal π -stacking mode. This mode, in principle, will produce the strongest π -electron overlapping with efficient charge transport along the π -stacking direction. But the ideal π -stacking is very difficult to form due to strong Coulombic repulsion between adjacent molecules, it often results in co-facial π -stacking, which in turns generates another two aggregation modes named as pitched π -stacking and rolled π -stacking, respectively (Fig. 1(b)). In these models, one molecule translates in parallel relative to another molecule along the long axis or short axis, termed pitch angle and roll angle, respectively. The π -electron overlapping can maintain to a large extent when the translation distance is small for these two cases, and molecular packing would follow the 1D π -stacking and 2D brick stacking mode with high carrier mobility along the π -stacking direction as shown in Fig. 1(c). However, these two cases combined with the ideal π -stacking usually exhibit severe quenching of optical properties, generating almost no light emission. Further increasing the pitch angle or rotating one molecule along its long axis leads to the change of molecular packing from “face-to-face” to “face-to-edge”, forming typical herringbone packing mode. This mode is beneficial for the balance of high carrier mobility and good light emission efficiency. Instead of rotating the long axis, the rotation of stacking axis of one molecule will maintain the parallelity between adjacent molecules (X-aggregation), and consequently leads to a cross dipole molecular packing in solid state. This model generally produces the strongest light emission due to miniaturized π -electron overlapping but significantly reduces the charge transport efficiency.

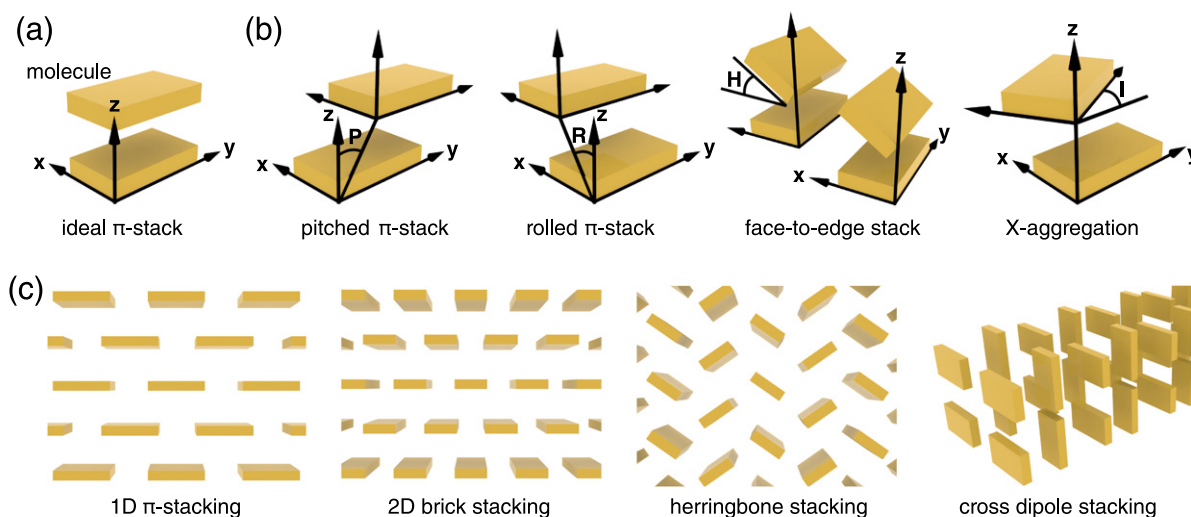


Fig. 1 Schematic drawing of molecular aggregation modes. (a) Ideal π -stack. (b) Non-ideal molecular aggregation modes. (c) Typical molecular packings in 3D assemblies.

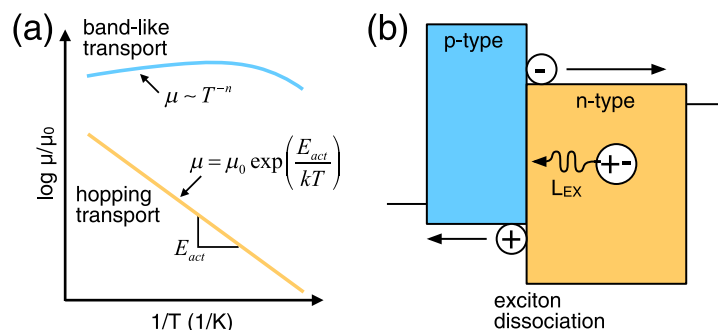


Fig. 2 (a) Electrical characteristics of charge transport models for organic semiconductors. (b) Schematic drawing of exciton generation, diffusion, and dissociation in an organic p-n junction.

Optoelectronic characteristics

The long-range ordered packing of molecules in organic single crystal creates significantly different optoelectronic properties compared to amorphous semiconductors. In this section, the unique optoelectronic characteristics of single crystal organic semiconductors, including the band-like charge transport and long exciton diffusion length are summarized.

In amorphous organic semiconductors, carriers are highly localized within one molecule. The charge transport for amorphous materials is dominated by hopping process, which means the carriers need to overcome an energy barrier so that they can excited from trapped states to transport energy level. The origin of traps may come from defects, grain boundaries or local inhomogeneity of materials. By assuming a single energy level of trapped charges, the charge transport can be described by the multiple trapping and releasing (MTR) model (Letizia *et al.*, 2010). In MTR model, the hopping process is driven by thermal energy, so the mobility can be described by Eq. (1):

$$\mu = \mu_0 \exp\left(\frac{E_{act}}{kT}\right) \quad (1)$$

where μ_0 is the mobility at an infinite temperature, E_{act} is the activation energy of the mobility, k is the Boltzmann constant, and T is the absolute temperature. It is concluded that the charge transport in amorphous organic semiconductors is thermally activated as shown in Fig. 2(a), in which higher temperature leads to higher carrier mobility.

The MTR model is no longer valid for most of single crystal organic semiconductors. Because of well-arranged molecules in organic crystal, carriers are delocalized over a few of molecules. Unlike inorganic single crystals such as silicon, the carrier delocalization for organic crystal is a lot weaker. But this phenomenon already alters the charge transport from hopping to band-like behavior. The temperature-mobility relationship of band-like transport is defined by the power law of $\mu \sim T^{-n}$, in which the reported n value ranges from 0.5 to 3 (Cho *et al.*, 2015; Liu *et al.*, 2011; Troisi, 2011). This relationship valid until at cryogenic temperature, in which case the extrinsic effects such as deep trap states become dominate (Fig. 2(a)).

Exciton diffusion length is critical for photovoltaic applications. The core structure of a conventional organic photovoltaic (OPV) device is the p-n junction. In an OPV device, excitons (electron-hole pair) are generated when under illumination, and then diffuse to the p-n junction interface before they are recombined as shown in Fig. 2(b). The dissociation of excitons occurs because of the energy difference at p-n junction interface and results in separated electrons and holes. Those electrons and holes transport to cathode and anode, respectively, and eventually generate electricity output. One of the key steps in above-mentioned process is exciton diffusion, the excitons contribute to electricity output only when they can reach the p-n junction interface, otherwise they will recombine without electrical energy conversion.

The averaged exciton diffusion length L_{EX} of amorphous organic semiconductors ranges from 10 to 50 nm. This value confines the film thickness of the OPV device thus limits the overall light absorption since the excitons are generally unable to travel to the p-n junction interface if one of the semiconductor layers is thicker than L_{EX} . The case is different in organic single crystal, a very large exciton diffusion length ($L_{EX} \sim 3\text{--}8\ \mu\text{m}$) in highly ordered rubrene single crystal has been observed experimentally (Najafov *et al.*, 2010). This finding indicates the great potential of high energy conversion efficiency of OPV based on organic single crystals.

Main Body: Materials, Processing, and Devices

Single Crystal Materials

To date, more than one hundred of organic small molecules have reported (Wang *et al.*, 2012) with intrinsic carrier mobility higher than amorphous silicon ($\sim 1\ \text{cm}^2\ \text{V}^{-1}\text{s}^{-1}$), and some of them demonstrate mobility over $10\ \text{cm}^2\ \text{V}^{-1}\text{s}^{-1}$ at the same time easy to grow high-quality crystal either by physical vapor transport or by solution process (He *et al.*, 2015; Jurchescu *et al.*, 2007; Minemawari *et al.*, 2011; Peng *et al.*, 2016; Takeya *et al.*, 2007). The chemical structure and reported mobility of some representative materials are shown in Fig. 3.

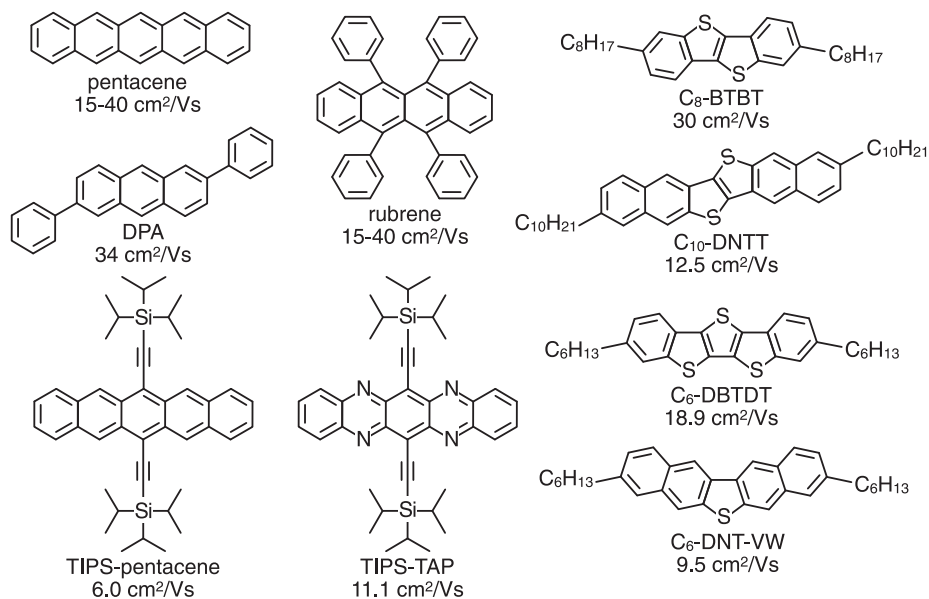


Fig. 3 Chemical structures of representative high mobility organic semiconductors discussed in the section.

Pentacene and other oligoacene derivatives such as rubrene are classical organic semiconductors with mobility up to 40 cm² V⁻¹s⁻¹ in single crystal form. The oligoacene core provides good intramolecular delocalization of electrons, and this delocalization is rapidly enhanced with increasing number of benzene rings. However, when the number of benzene rings is larger than six, the molecules show poor chemical stability. Oligoacene derivatives always show a typical herringbone molecular packing mode with good intermolecular π -electron overlapping and high transfer integral to achieve high mobility. The basic oligoacene derivatives including anthracene, tetracene, and pentacene are planar molecules, this characteristic brings good charge transport but limited solid emission. Our recent discovery shows that by incorporating a carbon-carbon single bond at 2,6-positions in anthracene, the molecule shows slightly torsion and will exhibit strong solid emission without sacrificing charge transport ability. Taking the representative 2,6-DPA molecule as an example, its single crystal shows carrier mobility as high as 34 cm² V⁻¹s⁻¹ at the same time has 41.2% photoluminescence quantum yield for blue light emission (Liu *et al.*, 2015). These types of materials hold great promise for novel optoelectronic applications including organic light emitting transistors (OLETs) or electrically pumped organic lasers.

To further improve the chemical stability, the thiophene units are introduced into the center of acene backbone, forming two high-mobility material systems, the BTBT derivatives and DNTT derivatives, respectively. The presence of thiophene units lowers the HOMO level of materials and greatly alters their chemical activity, thus bringing better resistance to oxygen and water when stored in ambient condition. For example, the DNTT based OFETs have shown ambient stability over one year reported by different groups, (Zschieschang *et al.*, 2011; Chen *et al.*, 2022) the maximum five years storage of OFETs without apparent performance loss have been observed by Prof. Li's group (Chen *et al.*, 2022). Both BTBT derivatives and DNTT derivatives can maintain herringbone molecular packing with or without side alkyl chains. The high mobility of 30 cm² V⁻¹s⁻¹ and 12.5 cm² V⁻¹s⁻¹ for C₈-BTBT and C₁₀-DNTT single crystal devices are achieved, respectively (Minemawari *et al.*, 2011; Peng *et al.*, 2016). Other thiophene based crystalline organic semiconductors also exhibit high mobility such as 18.9 cm² V⁻¹s⁻¹ for C₆-DBTDT and 9.5 cm² V⁻¹s⁻¹ for C₆-DNT-VW (He *et al.*, 2015; Okamoto *et al.*, 2013). The latter one has bent-shaped π -cores, which has higher radii of rotation and translation, beneficial to reduce the unfavorable molecular motion in the solid state. The dynamic disorder of organic molecules in the solid state, which may strongly disturb the charge transport, could be effectively suppressed by the bent-shaped molecular structure. More recent progress of bent-shaped organic semiconductors can be found elsewhere (Okamoto *et al.*, 2020).

Compared to herringbone molecular packing, the 2D brick stacking introduces even better π -electron overlapping to provide high carrier mobility but negligible light emission. A series of acene and heteroacene derivatives where two bulky solubilizing groups connected to the center of the acene core not only show high mobility of 6.0 cm² V⁻¹s⁻¹ for p-type TIPS-pentacene semiconductor (Hulea *et al.*, 2006) but also very high mobility of 11.1 cm² V⁻¹s⁻¹ for n-type TIPS-TAP semiconductor (Xu *et al.*, 2016b). The TIPS group allows close enough contact between adjacent molecules, and increases the solubility of acenes or heteroacenes, largely simplifying the fabrication process of OFET device.

Methods to Grow Organic Single Crystal

Different from inorganic single crystal in which the atoms are connected via strong covalent or ionic bonds, organic molecules aggregate through weak van der Waals force. The melting point and sublimation temperature of organic materials are much lower.

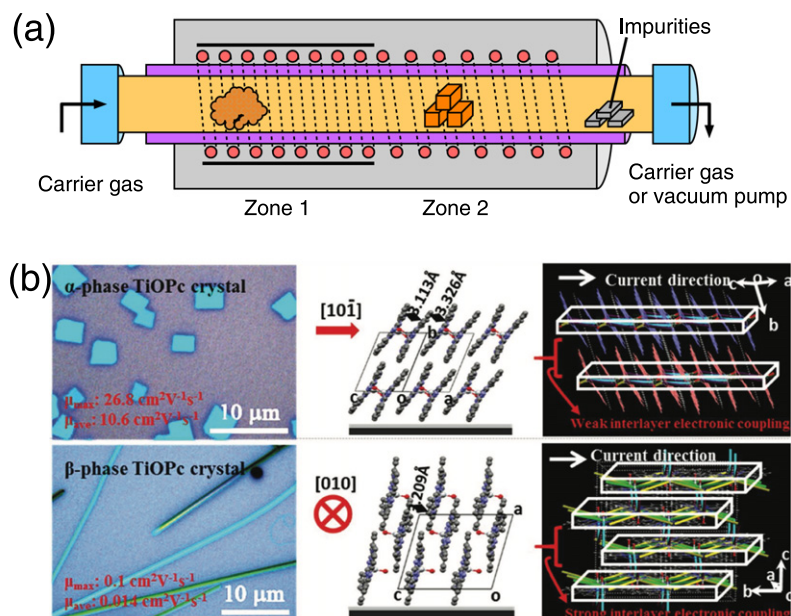


Fig. 4 (a) Schematic drawing of a physical vapor transport furnace. (b) Left: Optical microscopy images of the two phases with corresponding mobility information. Middle: Molecular arrangements of α - and β -TiOPc relative to the substrate. Right: Illustration of electronic coupling networks for α -microsheet, and β -nanoribbon crystals. Reproduced with permission. Zhang, Z.P., Jiang, L., Cheng, C.L., *et al.*, 2016b. The impact of interlayer electronic coupling on charge transport in organic semiconductors: A case study on titanylphthalocyanine single crystals. *Angewandte Chemie International Edition* 55, 5206–5209, Copyright 2016, Wiley-VCH.

In addition, a great number of organic materials can easily dissolve into common organic solvents, enabling solution processed crystallization. In this section, the representative vapor process and solution process to grow high-quality organic single crystal are introduced, other organic crystal growth methods can be found from several excellent reviews (Qu *et al.*, 2016; Wang *et al.*, 2018a).

Physical vapor transport

Physical vapor transport (PVT) is a typical vapor process for crystal growth, and its schematic diagram is shown in Fig. 4(a). PVT combines the crystal growth and material purification into one process. In the PVT process, the source material undergoes sublimation at high temperature and low pressure, the organic molecules inside a quartz tube are transported to the cooler side in a carrier gas, where crystallization occurs through oversaturation. Compared to chemical vapor deposition (CVD), there is no chemical reaction involved in the crystallization process. The purification process is applied by creating multiple temperature zones in the cooler side, different phases of organic material and impurities would condense separately at desired temperature zone. For example, Zhang *et al.* (2016b) obtained both α - and β -phase of high mobility TiOPc organic crystals by carefully tuning the temperature zones of furnace (Fig. 4(b)). It turns out that the thermodynamically stable α -phase is likely to condense at higher temperature zone while the kinetically stable β -phase is preferred to condense at lower temperature zone. In addition to TiOPc, various organic materials can crystallize by PVT method without considering the solubility. More information about PVT grown organic single crystals can be found elsewhere (Jiang and Kloc, 2013).

Solution processed organic semiconductor crystals

Other than PVT grown organic micro/nano crystals, the solution processing methods are preferred due to their low fabrication cost. The solution processed organic crystals are usually known as 2D crystals, since the lateral dimension of crystal (mm to cm scale) is significantly larger than the film thickness which ranges from monolayer to around 100 nm. The 2D organic crystals are desired for large-scale device array fabrication.

Solution shearing is one of the representative solution methods to grow high-quality, large area 2D organic crystals. The schematic drawing of solution shearing setup is shown in Fig. 5(a). The key to this method is that the liquid is confined in between the blade and substrate, forming a meniscus like liquid profile. By controlling the surface energy of the substrate, the small contact angle of liquid on the substrate leads to the maximum solvent evaporation flux occurring at the three-phase contact line. Therefore, the crystallization starts from the three-phase contact line, while at the same time, the blade moves horizontally away from the contact line with a constant velocity, allowing continuous crystal growing until it covers the whole substrate. The solvent evaporation induced directional convective flow in the liquid enhances the crystal growth and aligns the fastest growth axis with the coating direction. The viscous force originated from the velocity gradient in between the blade and the substrate is also helpful for large size crystal growth.

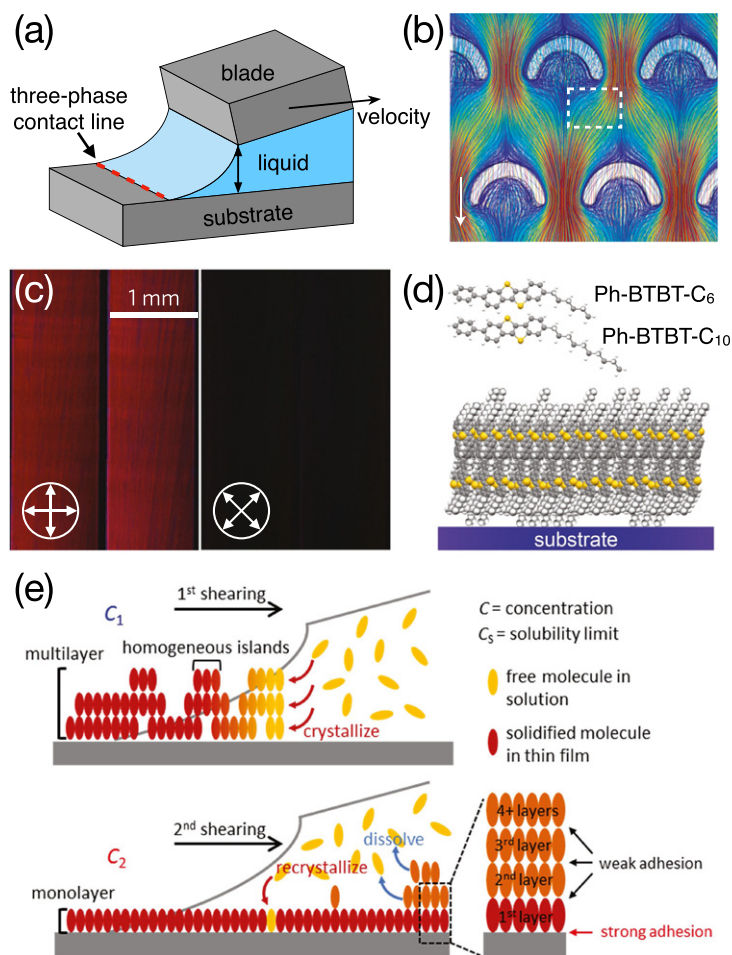


Fig. 5. (a) Schematic drawing of solution shearing setup. (b) Streamline representation of simulated fluid flow around the micropillars. The arrow indicates the flow direction. The streamlines are color coded to indicate the scale of velocity (mm s^{-1}), ranging from 0 (deep blue) to 1.3 mm s^{-1} . (c) Cross-polarized optical micrograph of a TIPS-pentacene film coated from its mesitylene solution with using FLUENCE, at a shearing speed of 0.6 mm s^{-1} . (d) Upper part, schematic for two kinds of Ph-BTBT-C_ns (π Core-C_n) with different alkyl chain lengths; lower part, schematic for layered mixed crystal of Ph-BTBT-C_n that embraces alkyl chain length disorder. (e) Schematic drawing of the dual-solution-shearing process. Dissolving (blue arrows) and recrystallization (red arrow) processes promote the growth of a highly crystallized semiconductor monolayer. Reproduced with permission from (b-c) Diao, Y., Tee, B.K., Giri, G., *et al.*, 2013. Solution coating of large-area organic semiconductor thin films with aligned single-crystalline domains. *Nature Materials* 12, 665–671, Copyright 2013, Springer Nature. (d) Arai, S., Inoue, S., Hamai, T., Kumai, R., Hasegawa, T., 2018. Semiconductive single molecular bilayers realized using geometrical frustration. *Advanced Materials* 30, 1707256, Copyright 2018, Wiley-VCH. (e) Peng, B.Y., Huang, S.Y., Zhou, Z.W., Chan, P.K. L., 2017. Solution-processed monolayer organic crystals for high-performance field-effect transistors and ultrasensitive gas sensors. *Advanced Functional Materials* 27, 1700999, Copyright 2017, Wiley-VCH.

Several strategies effectively improve the grown crystal quality to achieve large-scale, highly aligned and layer controlled organic single crystal thin films. Diao *et al.* (2013) demonstrated a silicon blade modified with sub-100 micrometer crescent-shaped micropillar structure to grow cm scale organic crystals. Fluid dynamic simulation suggests that the micropillars introduce lateral component in the flow and generate recirculation of the flow (Fig. 5(b)). These solvent flow behaviors enhance the later mass transport in the solution, which is critical for large-scale organic crystal growth. As a result, a centimeter scale TIPS-pentacene single crystal thin film is realized by this method as shown in Fig. 5(c). Arai *et al.* (2018) discovered the so-called geometrical frustration effect by properly mixing two small molecules with the same conjugated core but different alkyl chain length. For example, the organic solution consists of Ph-BTBT-C₆ and Ph-BTBT-C₁₀ molecules with mixing ratio of 1:9 would trigger the self-organization of molecules when performing the solution shearing and result in a single molecular bilayer (SMB) thin film structure up to wafer scale (Fig. 5(d)). Peng *et al.* (2017) showed that the multiple times shearing can largely suppress the out-of-plane layer thickness variation of sheared thin film (Peng *et al.*, 2017). By shearing on the same substrate twice with different solution concentration, a monolayer C₁₀-DNTT organic single crystal is demonstrated. The first time shearing always results in varied layer thickness, and the work of adhesion between C₁₀-DNTT and SiO₂ substrate is slightly larger than its value between C₁₀-DNTT interlayers, so the upper layers can be dissolved and recrystallize to fill the void in the first layer during second time shearing with a dilute solution, resulting in a large-area monolayer C₁₀-DNTT single crystal (Fig. 5(e)).

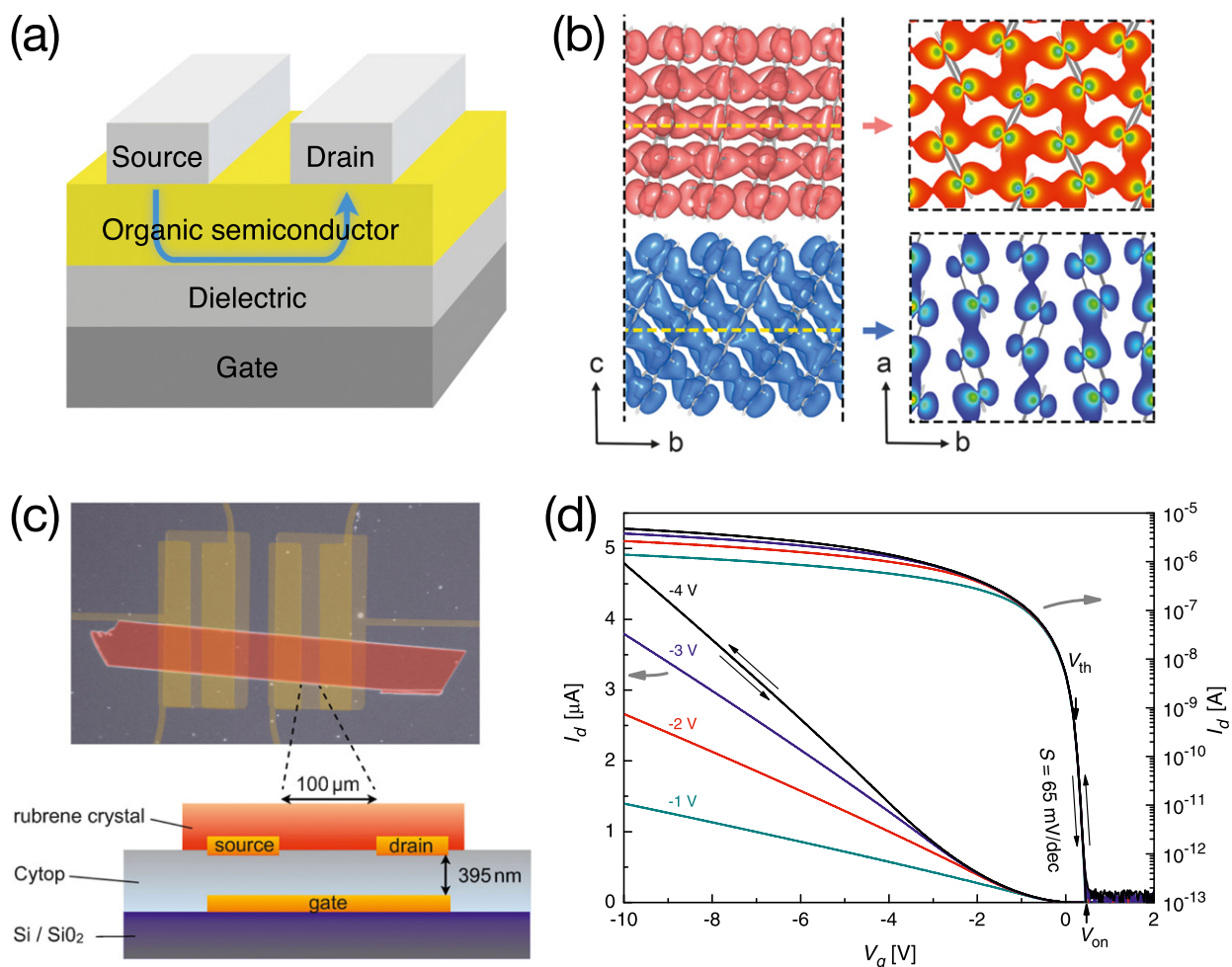


Fig. 6 (a) Schematic drawing of a top-contact bottom-gate organic field-effect transistor. (b) Visualized molecular orbitals of the intermolecular bonding contours of $0.00015e = \text{Bohr}^3$. Yellow dashed lines in the left figure indicate the positions of the slices. The top phenyl groups of the pentacene molecules are drawn in the right figure. (c) Colored photograph and schematic cross-section of the single-crystal OFET. The channel length and width are 100 and 270 μm, respectively. The thickness of the rubrene crystal is 2.3 μm. (d) Measured transfer curve of the rubrene single-crystal FET using a CYTOP layer as the gate dielectric. In the subthreshold regime (above $V_{th} = 0.23$ V), the exponential dependence of the currents on the gate voltage corresponds to a subthreshold swing of $S = 65$ mV decade⁻¹. Reproduced with permission from (b) Zhang, Y.H., Qiao, J.S., Gao, S., *et al.*, 2016a. Probing carrier transport and structure-property relationship of highly ordered organic semiconductors at the two-dimensional limit. *Physical Review Letters* 116, 016602, Copyright 2016, American Physical Society. (c–d) Blulle, B., Hausermann, R., Batlogg, B., 2014. Approaching the trap-free limit in organic single-crystal field-effect transistors. *Physical Review Applied* 1, 034006, Copyright 2014, American Physical Society.

In addition to solution shearing, another method named solution epitaxy demonstrates great potential to grow high-quality 2D organic single crystal (Xu *et al.*, 2016a). Instead of growing organic crystal on rigid substrate, a liquid state surface provides the platform for organic molecules to assembly. Organic solution is dipped onto an antisolvent solvent (i.e., water) and spreads under surface tension. Then the evaporation of organic solvent drives the molecules start to assemble due to strong π - π interaction, forming a number of tiny crystals or up to centimeter scale 2D organic crystals depending on the spreading condition, molecules type or other processing parameters (Wang *et al.*, 2018c). The fluidic nature of liquid state surface allows free movement of organic molecules therefore guarantee high-quality 2D crystal growth. The completed organic crystal can then be transferred onto any target substrate to construct single or heterojunction devices. OFETs, ambipolar transistors, and phototransistors have demonstrated by this method and show superior performance with the aid of high-quality 2D organic crystals.

Organic single crystal device

Organic field-effect transistor

Organic field-effect transistor (OFET) is the fundamental unit to construct large-scale integrated circuits. The conductive channel of OFET between source and drain electrodes is controlled by the third gate electrode through electric field. The conventional top-contact bottom-gate device configuration of OFETs is shown in Fig. 6(a). In OFET, two major processes are involved in device

operation, the charge transport in the channel region and charge injection from electrodes. Both processes are strongly influenced by the thin film morphology of organic semiconductor. For both processes, single crystal organic semiconductors are of great importance to improve the device performance because of their long-range ordered molecular packing, defect-free nature, atomic smooth surface morphology and controllable layer thickness. The detailed electrical characteristics of single crystal OFETs are discussed below.

One of the most important device parameters is the field-effect mobility. It is directly related to semiconductor/dielectric interface properties. During the OFETs operation, charge carries accumulate at the semiconductor/dielectric interface under the gate voltage, forming conductive channel within a few nanometers region and these charge carries migrate from source to drain along the interface under the electric field. Because the scope of this article is focusing on organic semiconductor, we assume the dielectric of OFET is good enough without bringing unknown influence on device performance. For crystalline organic semiconductor, charge transport exhibits band-like behavior due to higher degree of carrier delocalization. Zhang *et al.* (2016a) visualized the continuous network-like molecular orbitals in 2D pentacene organic crystal by using density function theory (DFT) as shown in Fig. 6(b).

Subthreshold swing (SS) of OFET is defined as how much the gate voltage required to modulate the drain-source current over one order of magnitude at subthreshold region. SS represents how fast the device could switch on and off. In addition, the off-state current at zero gate bias which reflects the static power consumption of OFET device, is directly determined by SS. Therefore, achieving small SS benefits low power application of OFETs. In the subthreshold region, I_{DS} is mainly driven by diffusion current, and the carrier concentration varies exponentially with gate voltage. Quantitatively, the SS is proportional to the trapped charge density below transport energy level, since the gate induced carriers must fill the trap states prior to contribute to channel current. Assuming zero trap states in bulk organic layer and semiconductor/dielectric interface, the theoretical minimum value of SS at room temperature ($T = 300$ K) is $59.5 \text{ mV decade}^{-1}$. The key to reduce SS is to eliminate the trap states located both in the bulk organic layer and at semiconductor/dielectric interface. Therefore, organic single crystal transistor is an ideal candidate to achieve extremely low SS because of its highly ordered molecular packing. The combination of highly crystalline organic semiconductor and an atomic flat dielectric surface produce extremely steep SS closing to theoretical limitation. A record low trap states density of $\sim 10^9 \text{ cm}^{-2} \cdot \text{eV}^{-1}$ is observed in rubrene single crystal, and $SS = 65 \text{ mV decade}^{-1}$ is achieved in the device as shown in Fig. 6(c, d), equivalent to one trap in every 10^8 rubrene molecules if assuming traps are evenly distributed in the bulk crystal (Blulle *et al.*, 2014). This result suggests that organic single crystal is a promising candidate for high-performance electronic devices with ideal “trap-free” characteristic.

Charge injection through electrode/semiconductor is another important process for OFET operation. Effective injection with Ohmic-like contact is essential for obtaining excellent performance of transistor device. However, a Schottky barrier exists in most cases of electrode/semiconductor contact in transistor devices according to Schottky-Mott rule, leading to large contact resistance. In addition, the bulk resistance of organic layer also contributed to contact resistance especially for top-contact device configuration. Peng *et al.* studied the relationship between layer thickness of organic single crystal and contact resistance (Peng *et al.*, 2020). A bilayer C_{10} -DNTT single crystal top-contact OFET shows relatively low contact resistance of $186 \Omega \cdot \text{cm}$ at saturation region. This value is satisfactory for top-contact OFET but can further reduce to $75 \Omega \cdot \text{cm}$ when applying monolayer C_{10} -DNTT single crystal as the active layer. This result demonstrates the layer thickness is critical to determine the bulk resistance due to the poor charge transport in vertical direction for this kind of materials. Further analysis suggests that even the alkyl chain length in C_x -DNTT derivative could affect the bulk resistance, an optimized alkyl chain length to balance the injection, transport, solubility, and thin film morphology would be necessary to develop.

Organic phototransistor

Photodetector (PD) is the device that convert optical energy to electrical energy, it has been widely applied for imaging, communication, and scientific research. There are two major types of device structure of PD, including diode, and phototransistor. The former one is based on photovoltaic effect which has lower detectivity and dynamic range due to limited external quantum efficiency (EQE). The phototransistor can reach EQE larger than 100% because of the field-effect amplification. In organic phototransistor, the incident light alters the threshold voltage of transistor by inducing traps in the channel or lowering the injection barrier, therefore exponentially increase the output channel current, resulting in several orders of magnitude improvement of device parameters such as photoresponsivity, dynamic range and specific detectivity.

According to the operating principle of organic phototransistor, single crystal semiconductor enhances the field-effect mobility and has longer exciton diffusion length, leading to efficient photocurrent generation, so the photoresponsivity which defined as the light induced current per incident optical power is greatly enhanced. Huang *et al.* reported a ultrahigh photoresponsivity of $3.1 \times 10^5 \text{ A W}^{-1}$ at UV light by using C_8 -BTBT single crystal phototransistor (Yuan and Huang, 2016). In addition to the current under illumination, the minimum current under dark is also critical for phototransistor since it determines the specific detectivity. The dark current of phototransistor is known as the noise level of the device, and thus the photo-generated current can be detected only if it is larger than the dark current. The detection limit determined by noise current is defined as noise equivalent power (NEP), and the detectivity D is the reciprocal of NEP. For practical applications, specific detectivity D^* is commonly applied with normalized device area and bandwidth. The major advantage of single crystal organic phototransistors is their monolayer thick active layer. 2D organic single crystal with only one molecular layer could realize fully depletion region under field effect, so it exhibits extremely low dark current. Wang *et al.* demonstrated a TFT-CN single crystal organic phototransistor for NIR light sensing (Wang *et al.*, 2018b). The average thickness of active layer is 4.8 nm grown by solution epitaxy, resulting in fully depletion of the channel and the dark current is around 0.3 pA. As a result, the highest reported specific detectivity of $6 \times 10^{14} \text{ Jones}$ is achieved in NIR region. The extremely high D^* associated with large photoresponsivity of $9 \times 10^4 \text{ A W}^{-1}$ of this device suggesting that the 2D organic single crystal phototransistors could outperform their silicon counterparts.

Future Directions

Although many organic materials show good crystallinity and high carrier mobility, the strong anisotropic charge transport is observed for most of materials due to nonsymmetric molecular packing. This anisotropic electronic property somehow induces large device-to-device variation in organic integrated circuit applications. Developing organic crystals with isotropic transport property in planar direction or even in all three dimensions would significantly simplify the design and fabrication of organic device array or would inspire novel device structure such as vertical transistors.

The carrier mobility of organic materials is comparable to oxide transistors, demonstrating great potential for display back-panel, integrated circuits applications. Rational design of new organic materials is necessary to break the π - π stacking distance limitation, so that the carrier mobility can largely improve. The development of new materials requires the optimization of intermolecular charge transport, suppression of molecular motion in solid state, chemical stability and solubility, and the synthesis route of new materials is expected to be simple and robust.

Solution processing represents the low fabrication cost which is one of the major advantages of organic electronics. To achieve all solution processed organic single crystal growth, especially the large-area, layer controlled organic single crystal and its high-resolution patterning techniques is of great importance for high-performance and highly uniform single crystal transistor array fabrication. To fabricate single crystal OFET integrated circuits entirely by solution process is meaningful for practical applications, this makes organic electronic devices a promising candidate for next-generation electronics in terms of both performance and cost.

Novel transferring method needs to develop for both fundamental study and practical applications. Unlike PVT or solution shearing that only one type of crystal formed during the process, transferring crystals from source substrate to target surface by direct mechanical manipulation offers possibility to create novel structures such as single crystal p-n junction, organic superlattice, chiral crystal stacks and many other heterostructures. Plenty of new device physics, new optoelectronic phenomena, new insight into organic electronics will be developed with the aid of crystal transferring method.

Conclusions

In summary, single crystal organic semiconductor plays an important role to realize high-performance organic electronic devices. The weak van de Waals interaction between organic molecules in the single crystals determines their unique molecular aggregation modes and optoelectronic properties. Various organic materials can grow high quality single crystals either by vapor process or by solution process and demonstrate maximum carrier mobility over $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. OFETs and other devices based on organic single crystals have shown excellent performance on par with their inorganic counterparts. Further development of new materials and new fabrication methods will bring a bright future to the application of organic electronics.

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Organic Electrolyte-Gated Transistors

Guan Ying Wang and Keryn Lian, Department of Materials Science and Engineering, University of Toronto, Toronto, ON, Canada
Ta-Ya Chu, Advanced Electronics and Photonics Research Centre, National Research Council Canada, Ottawa, ON, Canada

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Abstract

This article provides an up-to-date review of organic electrolyte-gated transistors. Beginning with an introduction to the fundamental components, mechanisms, configurations, and figures of merit for electrolyte-gated transistors, the article will then transition to an evaluation of the materials used, followed by an overview of past and current applications, ending with the identification of key challenges and opportunities for the organic electrolyte-gated transistor.

Introduction

Organic electrolyte-gated transistors (OEGTs) have attracted growing attention and research efforts in the last two decades. OEGTs provide a variety of advantages over MOSFETs and organic thin film transistors (OTFTs) including low-power operation, flexibility, and solution processability. These advantages make OEGTs a compatible candidate for printed electronics, enabling the high-throughput, cost-effective manufacturing of OEGTs for applications in areas such as wearables, sensors, and the Internet of Things.

The electrolyte dielectrics used in OEGTs are liquid, semi-solid, or solid-state ion-conducting materials which provide a large capacitance ($\sim 1\text{--}40\text{ }\mu\text{F cm}^{-2}$) via the electrical double layers (EDL) at the electrolyte-semiconductor and electrolyte-gate interfaces. This large capacitance induces comparable current to traditional OTFTs at low driving voltages, enabling the sub-2 V operation of OEGTs across an assortment of compatible material components, device architectures, and applications. Since the capacitance of the gate dielectric is provided by the EDLs at the electrolyte interfaces, the thickness of the layer of electrolyte has less impact, unlike OTFTs which use non-electrolyte dielectrics.

This article will cover the following topics:

- An introduction to the concept of organic electrolyte-gated transistors (OEGTs) (Section “Introduction”)
- A description of the fundamentals of OEGTs including their components, operational mechanisms, and configurations (Section “Fundamentals of OEGTs”)
- The commonly used electrolyte materials (aqueous, ionic liquid, ion gel, polyelectrolyte, polymer electrolyte) and their advantages and challenges (Section “OEGT Materials”)
- Applications for OEGTs in the areas of biological sensing, wearables, electrochromic displays, electronic textiles, and neuro-morphic computing (Section “OEGT Applications”)
- Challenges and future opportunities (Section “Challenges and Future Opportunities”)
- Summary (Section “Summary”)

Fundamentals of OEGTs

Components

OEGTs are made of four major components: the substrate, the semiconductor, the electrodes, and the dielectric. The substrate provides mechanical stability and electrical insulation for the OEGT. Often a flexible polymer substrate like polyethylene terephthalate (PET), polyethylene naphthalate (PEN), or polyimide (PI) is used. This is made possible by solution processable OEGT components requiring less than 300°C annealing which is below the glass transition temperature of some suitable polymers.

The semiconductor, also known as the “channel”, is where charge carrier accumulation and conduction occur. The semiconductor should have good film-forming ability, carrier mobility, environmental stability, and purity. There must also be good adhesion and compatibility between the semiconductor and electrolyte dielectric for efficient charge generation as well as good interfacial adhesion between the semiconductor and the electrodes for efficient charge injection. The two main classes of semiconductors are organic, which use π -conjugated carbon-based polymers and small molecules, and inorganic, which are predominantly metal oxides or 2D materials.

The electrodes are known as the “source”, “drain”, and “gate” electrodes. The selection of source and drain electrodes impact the charge injection and extraction from the semiconductor material. The carrier injection barrier between the electrodes and semiconductor should be small in order to obtain a low threshold voltage. The alignment of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the semiconductors are required to reduce the carrier injection barrier. The gate acts as a control to turn the transistor on and off. The conductivity of the semiconductor is controlled by the bias applied to the gate electrode, where a minimum bias known as the “threshold voltage” is required to induce charge accumulation at the interfaces of the semiconductor. The electrodes should also be highly conductive and compatible with other device components to prevent electrochemical reactions and degradation. Gold is the most widely used electrode material for its low

resistivity and high stability. However, there has been recent interest in silver electrodes due to their lower cost and printability with lower sintering temperature requirements (Mo *et al.*, 2019; Robin *et al.*, 2019), as well as interest in carbon-based electrodes such as graphene which provide high conductivity and printability (Hong *et al.*, 2014; Singaraju *et al.*, 2019).

Finally, the dielectric acts as insulation between the gate electrode and semiconductor to prevent shorting of the device. In OEGTs, the dielectric is an electrolyte with the unique role of providing a large capacitance at each of its interfaces to enable lower threshold voltages and lower voltage operation of the transistor compared to traditional OTFTs. The electrolyte should also have a large dielectric constant, good adhesion and compatibility with other components, high ionic conductivity and capacitance, low interfacial roughness, and environmental stability. The selection of the electrolyte not only impacts the capacitance of the device, but also the thin film morphology of the semiconductor and efficiency of carrier injection.

Configurations

The four basic configurations for transistors are shown in Fig. 1. These are known as top gate top contact (TGTC), bottom gate top contact (BGTC), top gate bottom contact (TGBC), and bottom gate bottom contact (BGBC). Instead of a thin film layer, TGTC devices may use a probe or wire as the top gate as depicted in Fig. 2(a). These four configurations provide their own advantages for different applications. The top contact devices have better electrical performance due to low contact resistance between the source and drain electrodes and a larger charge injection area between the source and drain electrodes and the semiconductor. Meanwhile, the bottom contact devices are easier to fabricate. The top gate devices may be more stable due to the insulation of the semiconductor layer.

In addition to the four basic configurations, there is also a side-gate (also known as co-planar) configuration OEGTs use where the source, drain, and gate electrodes are fabricated in the same plane as shown in Fig. 2(b). These side-gate devices are very simple to fabricate. Additionally, there are also vertical architectures which have the thin film layers stacked on top of each other such that it takes up very little space as shown in Fig. 3. The advantage of these is that it has a very short channel length which provides faster switching. However, this device architecture is not often used in OEGTs.

Mechanisms

When a voltage is applied to the gate electrode, the dielectric becomes polarized and ions will migrate and accumulate at the gate/electrolyte and electrolyte/semiconductor interfaces. This will induce charges in the semiconductor via the field effect. The induced charges form a conducting channel if the bias applied to the gate exceeds a threshold voltage (V_T), enabling current flow between the source and drain electrodes and turning the transistor from the “off” state to the “on” state.

The relationship between the current flow through the semiconductor and the voltage applied to the transistor can be described by the MOSFET model. The following equations will be given for a transistor. In the linear region, the current-voltage characteristics are given by Eq. (1). In this region, the gate voltage (V_G) is greater than V_T and the drain-source voltage (V_{DS}) is less than or equal to the difference between V_G and V_T .

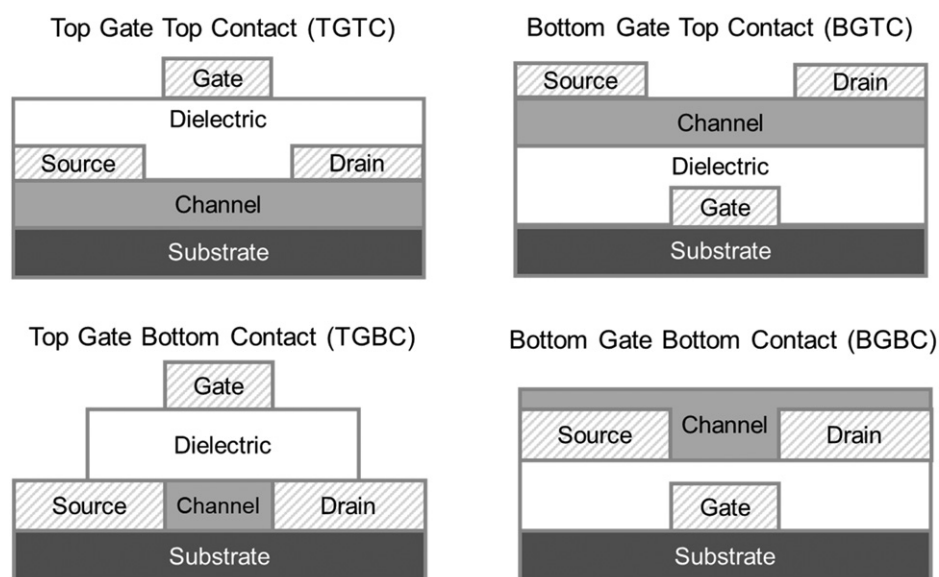


Fig. 1 Four general configurations for OEGTs. Modified with permission from Xu, Y., *et al.*, 2015. 'Development of high-performance printed organic field-effect transistors and integrated circuits'. *Physical Chemistry Chemical Physics* 17 (40), 26553–26574. Available at: <https://doi.org/10.1039/c4cp02413c>. Copyright 2015.

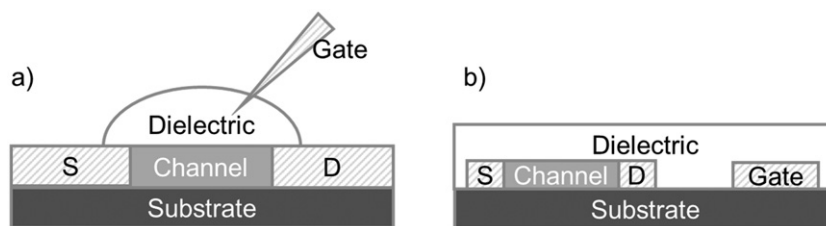


Fig. 2 Common OEGT architectures. a) Top gate bottom contact with liquid dielectric. b) side-gate, also known as in-plane or coplanar configuration.

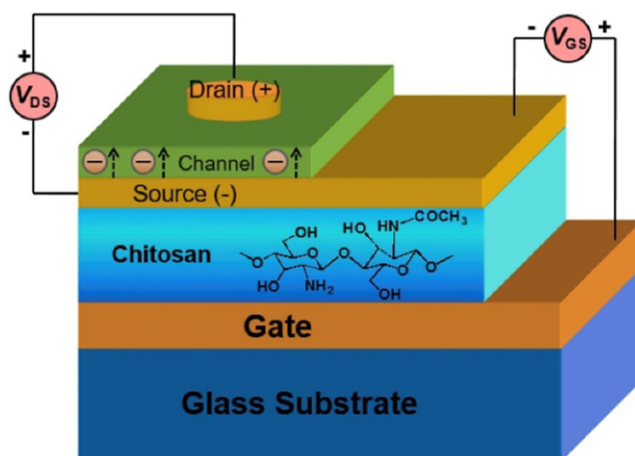


Fig. 3 An example of a vertical TFT. Reproduced with permission Hu, W., Zheng, Z., Jiang, J., 2017. 'Vertical organic-inorganic hybrid transparent oxide TFTs gated by biodegradable electric-double-layer biopolymer'. *Organic Electronics* 44, 1–5. Available at: <https://doi.org/10.1016/j.orgel.2017.02.001>. Copyright 2017.

$$I_{DS} = \frac{W}{L} \mu C (V_G - V_T) V_{DS} - \frac{V_{DS}^2}{2} \quad (1)$$

I_{DS} is the drain-source current, W is the channel (semiconductor) width, L is the channel length, μ is the semiconductor mobility, and C is the capacitance of the dielectric. The saturated current-voltage characteristics are given by Eq. (2). In this region, $V_G > V_T$ and $V_{DS} > V_G - V_T$.

$$I_{DS} = \frac{W}{2L} \mu C (V_G - V_T)^2 \quad (2)$$

From the saturation current-voltage relationship, when capacitance is increased, drain-source current can flow at much smaller applied voltages. This is an important advantage for OEGTs especially in printed electronics. Using electrolyte dielectrics can provide a high gating capacitance which can be three orders of magnitude greater than the common OTFT dielectric of SiO_2 . Therefore, OEGTs can be operated even below 1 V, enabling low-powered transistor applications.

When bias is applied to the transistor gate, the ions in the electrolyte are polarized. They form electrical double layers (EDLs) following a Stern-modified Gouy-Chapman diffuse double layer model as depicted in Fig. 4. At the interfaces (electrode/electrolyte and electrolyte/semiconductor), a monolayer of ions accumulates to form a Helmholtz layer. This EDL is very thin, approximately 1 nm, which permits the high gating capacitance (usually around $1\text{--}10 \mu\text{F cm}^{-2}$ in OEGTs) following Eq. (3):

$$C = \frac{\kappa \epsilon_0}{\lambda} \quad (3)$$

Where C is the capacitance, κ is the dielectric constant of the electrolyte, ϵ_0 is the vacuum permittivity constant, and λ is the Debye screening length (thickness of the EDL). Since the capacitance is highly dependent on the Helmholtz layer, the thickness of the electrolyte layer is not as important in OEGTs as commonly used polymer dielectric materials such as poly(vinyl alcohol) (PVA) or poly(methyl methacrylate) (PMMA). The EDL capacitance is a sum of the gate/electrolyte interface capacitance (C_{GE}) and the electrolyte/semiconductor interface capacitance (C_{ES}). The C_{GE} is usually much greater due to the larger contact interface. The capacitance of the EDL, C_{EDL} , can be given by Eq. (4):

$$C_{EDL} = (C_{GE}^{-1} + C_{ES}^{-1})^{-1} \quad (4)$$

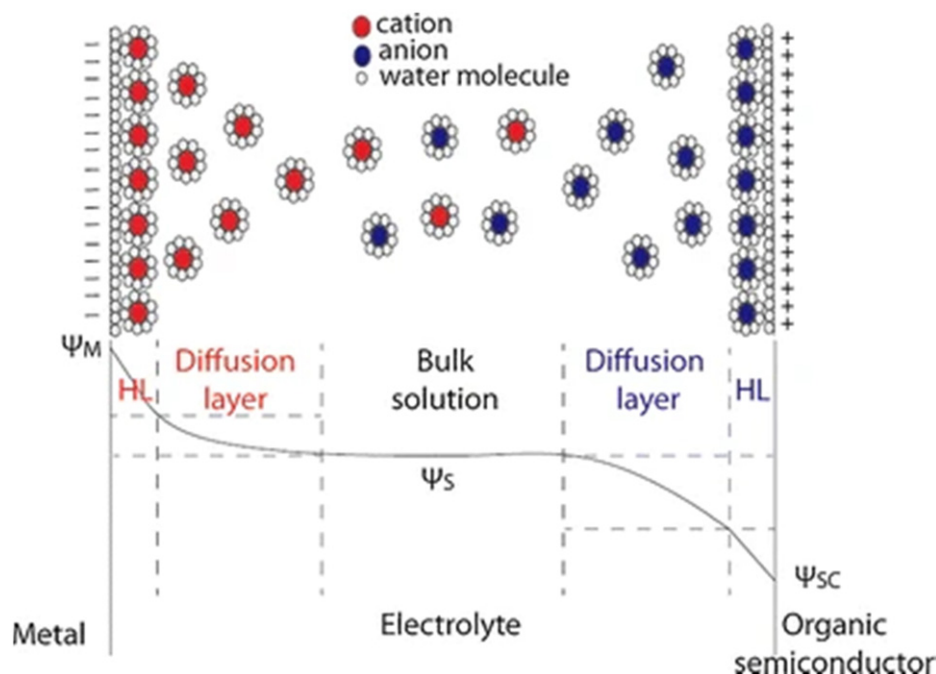


Fig. 4 Formation of Helmholtz layers at each electrolyte interface, with the potential distribution through the polarized electrolyte displayed. Reproduced with permission Kergoat, L., *et al.*, 2012. 'Advances in organic transistor-based biosensors: From organic electrochemical transistors to electrolyte-gated organic field-effect transistors'. *Analytical and Bioanalytical Chemistry* 1813–1826. Available at: <https://doi.org/10.1007/s00216-011-5363-y>. Copyright 2012.

Measurements and Figures of Merit

The figures of merit (FOMs) of OEGTs can be derived primarily from their characteristic current-voltage curves, known as the output and transfer curves. The transfer curve plots the source-drain current (I_{DS}) against the gate-source voltage (V_{GS}) at a constant source-drain voltage (V_{DS}) as shown in Fig. 5(a). The transfer curve shows the change in current as the gate voltage increases, and will show the transistor turning from an “off state” to an “on state”. From the transfer curve, FOM such as the threshold voltage, subthreshold swing, OFF current, and I_{ON}/I_{OFF} ratio can be obtained which are important for comparing between OEGTs. The output curve plots the I_{DS} against the V_{DS} at increasing gate-source voltage (V_{GS}) steps as shown in Fig. 5(b). The output curve shows the current saturation behavior of the device, which is dependent on the gate voltage.

Relevant to OEGTs, the most important figures of merit are threshold voltage V_T , OFF current, and I_{ON}/I_{OFF} ratio. For an OEGT, a V_T close to 0 V, an OFF current of at least 10^{-9} A or smaller, and an I_{ON}/I_{OFF} of 10^5 are preferred, although the experimental results depend on the materials chosen. Capacitance and ionic conductivity of the dielectric should also be considered. A larger capacitance will enable lower voltage operation of the device. Ionic conductivity is the speed of ion movement through the electrolyte. In the context of OEGTs, it is important to quickly form and dissociate EDLs. In the OEGT, fast ionic movement translates to a low switching time for the transistor which is desired for operation at higher frequency. In addition, hysteresis, a shift in measurements that occurs when sweeping the voltage back and forth which has been attributed to either the charge trapping/de-trapping from absorbed impurities in the semiconductor or dielectric, and the charge transport in the electrolyte following polarization (Gu *et al.*, 2005; Egginger *et al.*, 2009; Lee *et al.*, 2016), can drastically change the threshold voltage and should be monitored to ensure device stability.

Advantages and Potential Applications

There are three main advantages for OEGTs: their low voltage operation, solution processability, and ease of integration. Their low voltage operation which can be as low as sub-1 V comes from the use of the electrolyte gate dielectric that provides a high gating capacitance following the current-voltage relationship for OTFTs. The solution processability is derived from the types of materials used for OEGTs, including ion gels, polyelectrolytes, or polymer electrolytes which are often water-based and have the right viscosity and stability for printing technologies such as inkjet or aerosol jet printing. The solution processability of OEGTs makes them an attractive option for printed electronics. The ease of integration of the OEGT into complex circuits and sensing platforms also increases the attractiveness of OEGTs for many applications such as e-textiles, wearables, and especially biosensing.

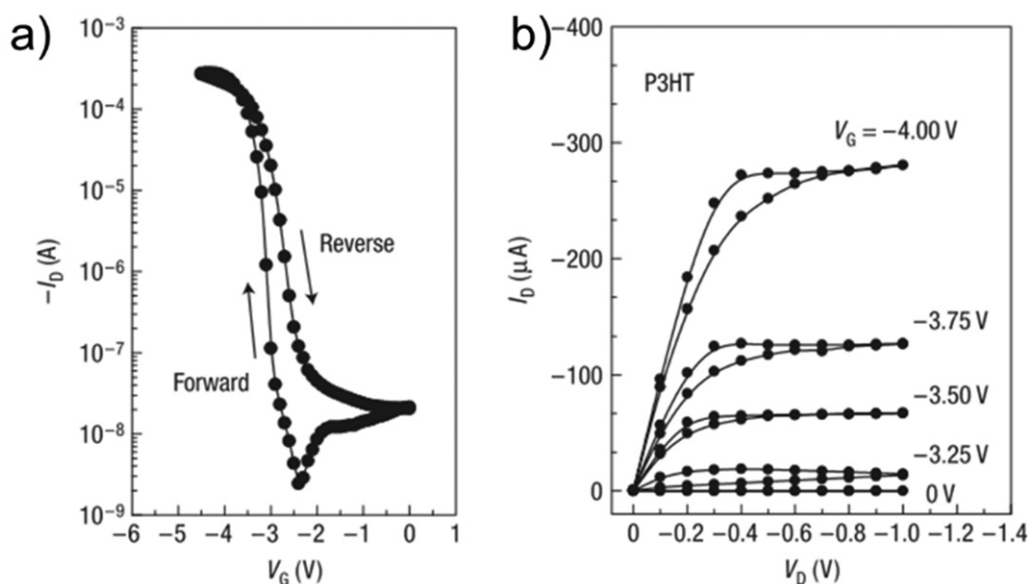


Fig. 5 P3HT ion gel-gated OEGT a) transfer curve and b) output curves. Reproduced with permission Cho, J.H., *et al.*, 2008. 'Printable ion-gel gate dielectrics for low-voltage polymer thin-film transistors on plastic'. *Nature Materials* 7 (11), 900–906. Available at: <https://doi.org/10.1038/nmat2291>. Copyright 2008.

OEGT Materials

As the key component in OEGTs, the electrolyte gate dielectric should have electrochemical compatibility with all other components of the OEGT, have good film-forming abilities, and can provide a high gate capacitance as well as sufficient electrical insulation. The common electrolyte dielectrics used in OEGTs can be divided into five different categories: aqueous electrolytes, ionic liquids (ILs), ion gels, polyelectrolytes, and polymer electrolytes.

Aqueous Dielectrics

Aqueous electrolytes such as water or a salt solution can function as gate dielectrics. Water itself is an effective gate dielectric due to its high κ -constant of approximately 80. TGBC device architectures are often used for aqueous dielectrics, especially the designs where the top gate is a metal wire or rod inserted into a reservoir of electrolyte as depicted in **Fig. 6**. Usually, this reservoir is a polydimethylsiloxane (PDMS) well which contains the electrolyte. Side-gate devices have also been used. In addition to pure water, salt solutions such as phosphate-buffered saline (PBS) have also been used as the electrolyte to increase the ionic conductivity of the solution or in the case of biological sensing applications, mimic human body fluids. Nonetheless, the added ions may lead to penetration of the semiconductor which lowers the overall performance of the device (Lago *et al.*, 2018).

It has been noted that water-gated transistor devices may have lower mobility compared to transistors with non-electrolyte gating. In an example with a rubrene semiconductor, a water-gated device reported a low hole mobility of $0.067 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Kergoat *et al.*, 2010). The mobility of rubrene in OTFT devices was reported to be usually orders of magnitude higher (Chen and Shih, 2009; Sim *et al.*, 2018). This effect was suggested to be a result of mobility degradation. Due to the large capacitance of water, the charge carrier distribution in the electrolyte is compressed more to the interfaces, leading to more sensitivity to surface roughness and defects, thus lowering mobility.

Water-gated transistors that are gated with salt solutions also suffer severely from unwanted ionic penetration into the semiconductor. One remedy is to use polymer chains in the semiconductor or electrolyte to form a barrier at the interface. For example, a NaCl-gated transistor used poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene) (pBTTT) semiconductor to achieve a mobility of $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a specific capacitance of $0.9 \text{ } \mu\text{F cm}^{-2}$. The elongated alkyl chains in pBTTT effectively formed a barrier at the semiconductor/electrolyte interface to prevent water penetration into the semiconductor layer. This is useful as salt solutions are often desired as an electrolyte gating medium to mimic biological environments for sensing applications.

Table 1 displays some aqueous electrolytes which have been used in organic OEGTs. Many water-based OEGTs use a TGBC architecture, with a probe acting as the top gate. The reported capacitances from the literature range from 0.9 to $3.8 \text{ } \mu\text{F cm}^{-2}$ which enabled the transistors to operate at driving voltages $< 10.51 \text{ V}$.

There are several advantages for aqueous electrolytes as they are easy to synthesize, often requiring just simple stirring. The devices are easy to set up and clean, and are compatible with microfluidic setups. In the case of biological sensing, aqueous electrolytes also allow for the direct functionalization of receptors to the gate or semiconductor surface in the electrolyte media.

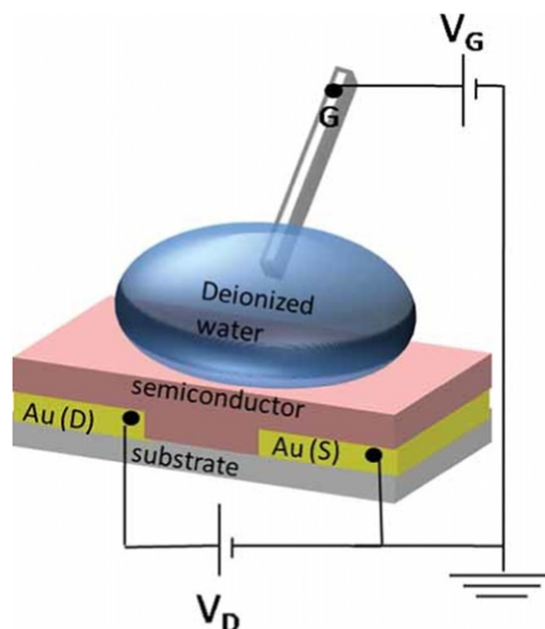


Fig. 6 A top gate bottom contact electrolyte-gated transistor, where the top gate is a wire inserted into a drop/reservoir of electrolyte (in this case water). Reproduced with permission Kergoat, L., *et al.*, 2010. 'A water-gate organic field-effect transistor'. *Advanced Materials* 22 (23), 2565–2569. Available at: <https://doi.org/10.1002/adma.200904163>. Copyright 2010.

Table 1 Aqueous electrolyte-gated field effect transistors

Dielectric	C ($\mu\text{F cm}^{-2}$)	Semiconductor	SD/Gate	V_T (V)	I_{ON}/I_{OFF}	I_{OFF} (A)	μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	V_{DS}
Water (Kergoat <i>et al.</i> , 2010)	3	P3HT	Au/Au	−0.16	150	N/A	5.9×10^{-3}	−0.5
Water (Kergoat <i>et al.</i> , 2010)	3	Rubrene	Au/Au	−0.09	8×10^4	10^{-11}	6.7×10^{-2}	−0.5
Water (Porrazzo <i>et al.</i> , 2014)	0.9	PBTTT (non-annealed)	Au/W tip	0	10^2	10^{-2}	0.06	−0.2
Water (Lago <i>et al.</i> , 2018)	3.8	TIPS-pentacene	Au/Pt wire	−0.140	100	10^{-10}	0.013	−0.2
Dulbecco's PBS (Lago <i>et al.</i> , 2018)	1.75	TIPS-pentacene	Au/Pt wire	0.05	100	10^{-9}	1.7×10^{-3}	−0.2
Water (Toss <i>et al.</i> , 2014)	4	P3HT	Au/Au	N/A	N/A	N/A	0.3×10^{-3}	N/A
Water (Toss <i>et al.</i> , 2014)	19	P3HT-COOH15	Au/Au	N/A	N/A	N/A	0.7×10^{-3}	N/A

However, aqueous electrolytes possess several disadvantages for use in OEGTs. They are environmentally unstable, prone to evaporation and weak against changes in temperature and humidity. Their viscosities are too low to be solution printed using methods such as inkjet or aerosol jet printing, limiting their potential in printed electronics. Deionized and salt solutions also may not be compatible with penetrable semiconductors such as the conjugated polymer P3HT, leading to low charge carrier mobility or semiconductor degradation as a result of ion penetration. In addition, they are not really portable due to their fluid nature and are not suitable for portable or wearable devices. Furthermore, pure water has low conductivity, as small as $5.5 \times 10^{-5} \text{ mS cm}^{-1}$ which will lead to slow EDL formation and dissociation, translating to a slow switching speed of the OEGT. Even when the ionic conductivity is improved by the addition of salts, this may lead to ionic penetration of the semiconductor which will degrade the device performance. Nevertheless, aqueous electrolytes are still widely used as a gate dielectric due to its very facile setup and good performance, especially in biological sensing.

Ionic Liquid Dielectrics

Ionic liquids (ILs) are a solventless composition of ions with a relatively low melting temperature, making them molten salts at room temperature. These ionic liquids are often made of nitrogen-containing organic cations and inorganic anions (Misra *et al.*, 2007). Common cation bases (where R_x is an alkyl chain) and anions for ILs are shown in Fig. 7. They are highly polar, possess a high ionic conductivity, and are thermally and electrochemically stable which makes them a promising candidate as a gate dielectric in OEGTs. Their high ionic conductivity enables a high switching speed for OEGTs.

The ILs used in some OEGTs are shown in Table 2. Some of the more popular combinations for ILs are 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) and Diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ([DEME][TFSI]). For the device architecture, the TGBC architecture was used often, although BGTC devices have also been fabricated.

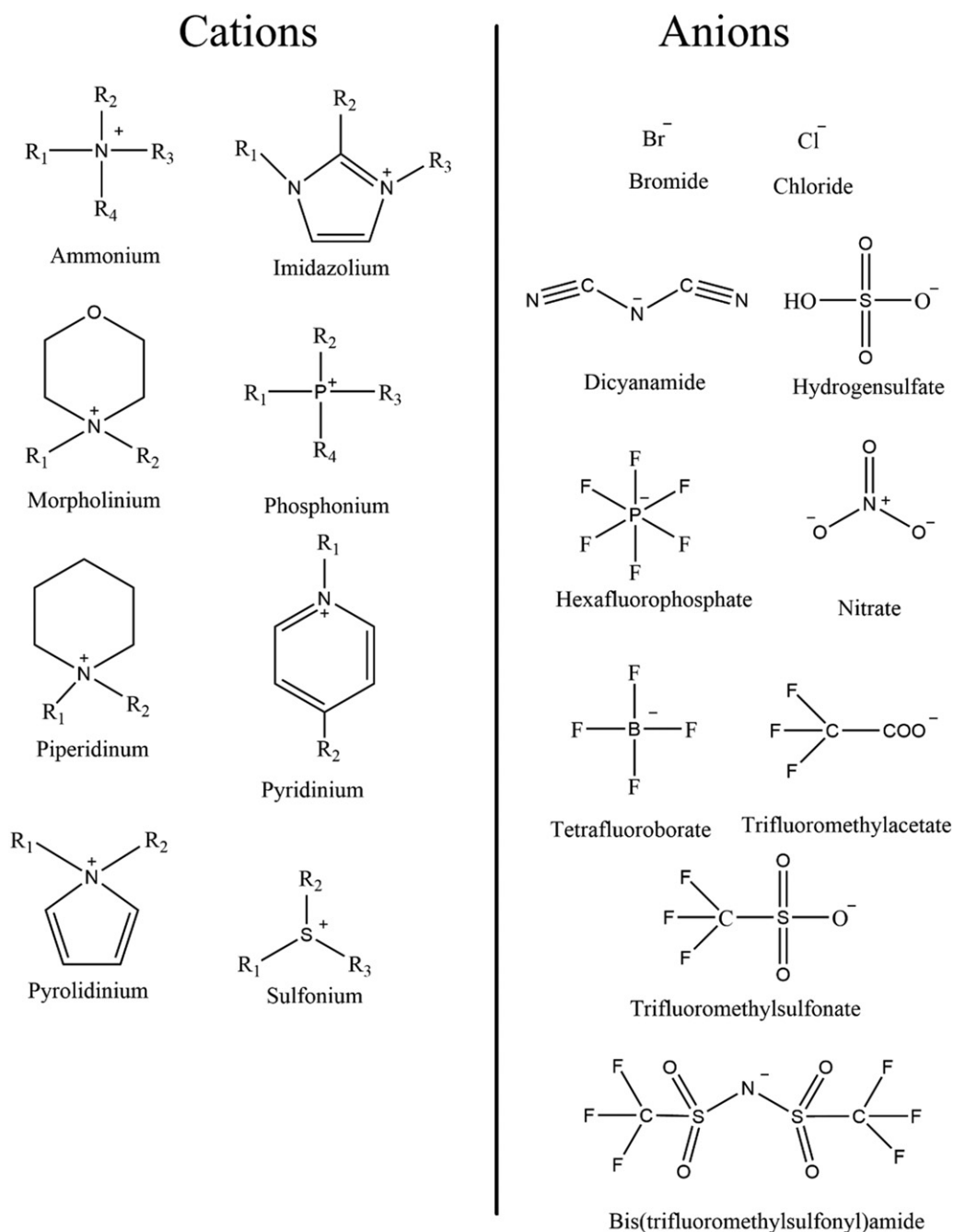


Fig. 7 Common cations and anions for ionic liquids.

One of the benefits of ILs are that they are highly tunable. Changes to the IL structure result in changed properties such as capacitance, morphology, and stability which will affect their performance in OEGTs. For example, different pairings of cations and anions may have different interactions with the semiconductor or result in changes in operational stability (Yadav *et al.*, 2021). Even the addition of four fluorine atoms between [EMIM][TFSI] and 1-ethyl-3methylimidazolium bis(fluorosulfonyl)imide ([EMIM][FSI]) can result in markedly different capacitance profiles as shown in Fig. 8 (Ono *et al.*, 2008). Ono *et al.* found that [EMIM][FSI] had a larger hysteresis than the [EMIM][TFSI]-gated device. This was attributed to a difference in interfacial interactions due to the additional fluorine atoms which may result in additional hole traps from impurities or absorption of moisture (Ono *et al.*, 2008).

Ionic liquids have also been shown to be compatible with both p- and n-type transistors. For example, Uemura reported the fabrication of IL-gated transistors using tetracyanoquinodimethane (TCNQ), a p-type semiconductor, and C60, an n-type semiconductor (Uemura *et al.*, 2010). The IL used was [EMIM][TFSI] with a capacitance of $5 \mu\text{F cm}^{-2}$ and ionic conductivity of 10 mS cm^{-1} (Uemura *et al.*, 2008).

Table 2 Ionic liquid-gated field effect transistors

Dielectric Material	Capacitance ($\mu\text{F cm}^{-2}$)	Ionic Conductivity (mS cm^{-1})	Configuration	Semiconductor	SD/Gate	V_T	I_{ON}/I_{OFF}	I_{OFF} (A)	μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	V_{DS}
[EMIM][TFSI] (Ono <i>et al.</i> , 2008)	11	20–30	Probe TGBC	Single crystal rubrene	Au/Au wire	N/A	N/A	N/A	0.41	–0.5
[EMIM][FSI] (Ono <i>et al.</i> , 2008)	5.4	20–30	Probe TGBC	Single crystal rubrene	Au/Au wire	N/A	N/A	N/A	1.2	–0.5
[EMIM][TFSI] (Uemura <i>et al.</i> , 2010)	5	N/A	BGTC	TCNQ	Au/Au	N/A	N/A	N/A	0.54	0.5
[EMIM][TFSI] (Uemura <i>et al.</i> , 2010)	5	N/A	TGBC	C60	Au/Au	0.4	103	10–11	0.04	–0.5

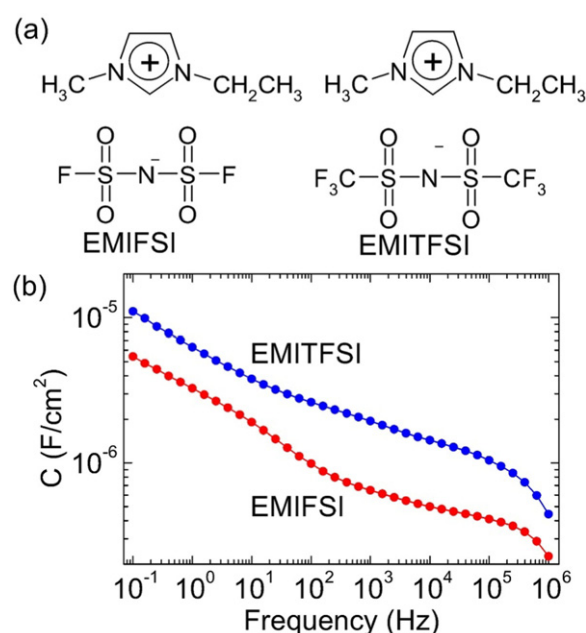


Fig. 8 The chemical structures of the ionic liquids (top left) [EMIM][TFSI] and (top right) [EMIM][FSI], showing a difference of two fluoro groups in the chemical structure. The frequency-dependent capacitance (bottom) of the ionic liquids. Reproduced with permission Ono, S., *et al.*, 2008. 'High-mobility, low-power, and fast-switching organic field-effect transistors with ionic liquids'. *Applied Physics Letters* 92 (10), 103313. Available at: <https://doi.org/10.1063/1.2898203>.

This demonstration of compatibility of ILs with the less common organic n-type semiconductor allows for the realization of n-type transistors for integrated circuit applications using ILs.

While ILs have shown great chemical and mechanical properties as well as good results in devices, there are still some limitations. Similar to aqueous electrolytes, ILs are in a liquid state and thus not very portable and not compatible with some printing processes. Although they are thermally and electrochemically stable, many ILs are air or moisture sensitive and reactive when not under inert conditions. There are also concerns about the high cost, complexity, and energy investment in synthesizing ILs (Wang *et al.*, 2016). Furthermore, there have been many environmental concerns regarding ILs which are often toxic and corrosive. For example, [EMIM][TFSI], a popular IL for OEGTs is a known toxin and environmental hazard. Another IL, [C4mim][PF₆], degrades to form hydrofluoric acid (Swatosloski *et al.*, 2003). Thus, while ILs do have good electrochemical and thermal properties, they are also hazardous and may not possess the mechanical requirements for some OEGT applications.

Ion Gel Dielectrics

Ion gels are a polymer matrix blended with IL, creating a solid-state composite electrolyte. The IL acts as a plasticizing salt, providing high ionic conductivity, thermal and electrochemical stability, and fast EDL formation. The EDL formation stems from

both high concentration of ionic species and ion movement which may be decoupled from polymer segmental motion. The polymer acts as a matrix, providing high mechanical strength and flexibility. The specific capacitance of ion gel dielectrics ranges from 1 to 40 $\mu\text{F cm}^{-2}$ and the ionic conductivity ranges between 1 and 10 mS cm^{-1} .

Ion gels can be physically or chemically crosslinked and are thus known as “chemical ion gels” or “physical ion gels”. Physical ion gels are formed through noncovalent interactions. They are commonly made using ABA or ABC triblock copolymers with a soluble middle block and insoluble end blocks, offering high tunability of the components and facile synthesis. Chemical ion gels are formed through covalent interactions and are often more difficult to synthesize as it is difficult to control the chemical crosslinking process to obtain the desired morphology and gelation level.

Physical ion gels consist of polymers such as polystyrene (PS), polyethylene oxide (PEO), and polymethyl methacrylate polymers (PMMA), and ILs such as [EMIM][TFSI]. For example, PS-PEO-PS triblock copolymers with [EMIM][TFSI] IL is a common ion gel for OEGTs. One reported by Cho *et al.* achieved a specific capacitance of 20 $\mu\text{F cm}^{-2}$ and an ionic conductivity of 8 mS cm^{-1} (Cho *et al.*, 2008). These characteristics, especially the high ionic conductivity, were made possible by the low gelation point of the ion gel, enabling good electrical performance of the OEGT.

Control of semiconductor morphology in combination with ion gels were reported to result in high performance of the OEGT. One way to improve the semiconductor morphology is to optimize the thickness and post-annealing process of the semiconductor layer, especially in ion-penetrable semiconductors like P3HT. In an example using PS-PMMA-PS with [EMIM][TFSI] IL ion gel and P3HT semiconductor, the semiconductor's improved film morphology coupled with a high-performance ion gel led to good transistor performance in many figures of merit (Kim *et al.*, 2013). Another approach is to focus on the structural design of the semiconductor. An increase in crystallinity and larger crystal domain sizes will also lead to higher mobility and high performance OEGTs when combined with an advanced ion gel gate dielectric. For example, an ion gel electrolyte based on poly(vinylidene difluoride-trifluoroethylene) (PVDF-TrFE)/poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) with [EMIM][TFSI] IL was reported to have a high capacitance of up to 4.9 $\mu\text{F cm}^{-2}$ (Nketia-Yawson *et al.*, 2018). The polymer semiconductor was designed to have crystalline domains with strong intermolecular chain interactions in an edge-on orientation for high mobility of over 5 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. The performance of the device was attributed to the good electrical properties of the ion gels which enabled strong polarizability of the gate dielectric, design of the semiconductor, and low contact resistance from the optimization of the device geometry.

For chemically-crosslinked ion gels, the very first examples used direct polymerization of PMMA monomer in [EMIM][TFSI] IL in the presence of a small amount of crosslinking agent (Susan *et al.*, 2005). Other chemical ion gels have been developed through the covalent linkage of monomers through polyaddition reactions or free radical polymerization. Interests in obtaining ion gels suitable for OEGTs as in the case of physical ion gels have sparked some efforts in facile chemical synthesis. Jeong *et al.* have developed a printable chemical ion gel using PVA polymer backbone, (poly)ethyl methacrylate (PEMA) chemical crosslinker, and [EMIM][OTf] IL in DMSO which has been demonstrated to be compatible with inkjet printing and controllable through the optimization of component ratios (Jeong *et al.*, 2019, 2020). As the ion gel is printed onto a heated substrate, the excess DMSO evaporates and the PVA and PEMA via a spontaneous ring-opening and esterification reaction to form a high-performance ion gel that does not require additional treatment such as UV-curing. A schematic of the ring-opening reaction is presented in Fig. 9.

The performance of some ion gels used in OEGTs in the literature are displayed in Table 3. The device architecture used is often TGBC, as it is simpler to cast the ion gel on top of the semiconductor and electrode layers, and it provides enough mechanical stability to cast the top gate. The main advantages of using ion gels are their fast EDL formation, good electrical properties, and solution processability. However, they are also susceptible to changes in humidity and temperature, resulting in long-term stability concerns.

Polyelectrolyte Dielectrics

Polyelectrolytes are polymers with ionizable groups in the backbone. These ionizable groups can dissociate and become mobile in solution. Depending on the charge of the backbone, they can form polycations or polyanions. The specific capacitance is usually in

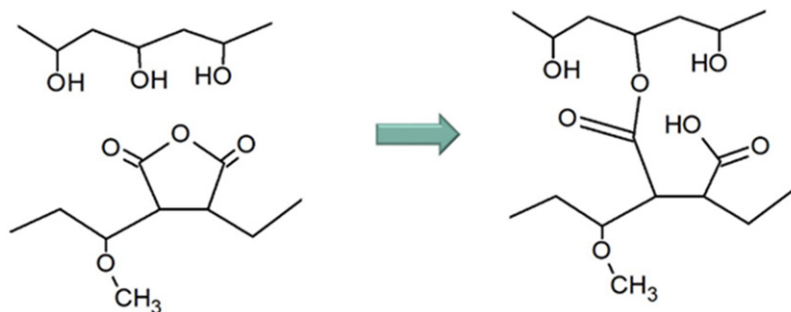


Fig. 9 Ring-opening esterification reaction of PVA and PEMA. Reproduced with permission Jeong, J., *et al.*, 2020. ‘Adhesive ion-gel as gate insulator of electrolyte-gated transistors’. ChemElectroChem 7, 2735–2739. Available at: <https://doi.org/10.1002/celec.202000305>. Copyright 2020.

Table 3 Ion gel-gated field effect transistors

Dielectric Material	C ($\mu F\ cm^{-2}$)	Ionic conductivity ($mS\ cm^{-1}$)	Configuration	Semiconductor	SD/Gate	V_T (V)	I_{ON}/I_{OFF}	I_{OFF} (A)	μ ($cm^2\ V^{-1}\ s^{-1}$)	SS ($mV\ dec^{-1}$)	V_{DS}
PS-PEO-PS, [EMIM][TFSI] (Cho <i>et al.</i> , 2008)	20	8	TGBC	P3HT	Au/Au	− 2.7	10^5	10^{-8}	1.8 0.7	100	− 1
PA6, [EMIM][TFSI] (Cho <i>et al.</i> , 2020)	10.5 (1 Hz)	1.8 (10^6 Hz)	TGBC	P3HT	Au/PEDOT:PSS	N/A	3.14×10^5	10^{-10}	2.83 0.20	N/A	− 0.1
PS-PMMA-PS, [EMIM][TFSI] (Kim, Hong, Lee, <i>et al.</i> , 2013)	162	N/A	TGBC	P3HT	Au/PEDOT:PSS	− 0.3	10^6	10^{-10}	1.3	66	− 0.8
PVDF, [EMIM][TFSI] (Cho <i>et al.</i> , 2018)	31	9.1 0.5	TGBC	P3HT	Au/PEDOT:PSS	N/A	10^5	10^{-9}	2.81	N/A	− 0.1
Poly(<i>t</i> BA- <i>r</i> -A22-4), [EMIM][TFSI] (Yoo <i>et al.</i> , 2020)	1	1.1	TGBC	P3HT	Au/PEDOT:PSS	− 0.2	8.4×10^4	1.9×10^{-9}	1.25	N/A	− 0.1
PVDF, [EMIM][TFSI] (Yang <i>et al.</i> , 2017)	25	2.9 0.7	TGBC	P3HT	Au/PEDOT:PSS	N/A	10^5	10^{-9}	2.9 0.82	81	− 0.5
P(VDF-HFP), [EMIM][TFSI] (Na and Kim, 2019)	6.11 0.22	N/A	TGBC	P3HT/IL CF 5 vol%	Au/PEDOT:PSS	− 0.02 0.04	1×10^4	10^{-6}	2.36 0.24	N/A	− 1
P(VDF-TrFE)/P(VDF-HFP)/[EMIM][TFSI] (Nketia-Yawson <i>et al.</i> , 2018)	4.9	N/A	TGBC	PDFDSe	Au/Au	− 0.98 0.06	10^5	10^{-8}	19.58	N/A	− 2
P(VDF-HFP)/[EMIM][TFSI] (Bae and Kim, 2020)	N/A	N/A	TGBC	C8-BTBT/PTAA	Au/PEDOT:PSS	0.078	8×10^2	10^{-8}	4.5×10^{-3}	N/A	− 1

Table 4 Polyelectrolyte-gated field effect transistors

Dielectric Material	C ($\mu\text{F cm}^{-2}$)	Configuration	Semiconductor	SD/Gate	V_T (V)	$I_{\text{ON}}/I_{\text{OFF}}$	I_{OFF} (A)	μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	V_{DS}
PS-PIL-PS, PIL = [EMIM][TFSI] (Choi <i>et al.</i> , 2015)	1	TGBC	P(NDI2OD-T2) ^a	Au/Au	0.4	2×10^3	5×10^{-10}	0.008	1
PSSH (Said <i>et al.</i> , 2006)	20	TGBC	P3HT	Au/Ti	−0.14	200	3×10^{-9}	0.0039	−0.8
PSSH, isopropanol, water (Thiburce and Campbell, 2016)	10	BGTC	P3HT	Au/Au	0.1	0.05	60	0.5×10^{-6}	0.16
P(VPA-AA) (Herlogsson <i>et al.</i> , 2007)	20	TGBC	P3HT	Au/Ti	−0.29	140	10^{-8}	0.012	−1
PAA:PEG (40 wt% PEG) (Liu <i>et al.</i> , 2019)	0.79	TGBC	PIDT-BT	Au/Au	−0.36	10^4	10^{-6}	0.12	−0.7

^aIonic conductivity of approximately $1 \times 10^{-3} \text{ mS cm}^{-1}$ was reported (Choi *et al.*, 2015).

the range of $1\text{--}10 \mu\text{F cm}^{-2}$. Additionally, polyionic liquids (PILs) are a type of polyelectrolyte which use ionic liquid monomer instead of a solid salt monomer that also belongs to this class. Common types of polyelectrolytes that have been used are polyacrylic acid (PAA) and polystyrene sulfonate (PSS).

One of the advantages of polyelectrolytes is the reduction of penetration into the semiconductor channel due to immobilization of the anion or cation. For example, Herlogsson *et al.* presented a P(VPA-AA) random copolymer of vinyl phosphoric acid and acrylic acid polyelectrolyte that had a specific capacitance of $20 \mu\text{F cm}^{-2}$. The resulting OEGT demonstrated an $I_{\text{ON}}/I_{\text{OFF}}$ ratio of 140, OFF current of approximately 10^{-8} A , and hole mobility of $0.012 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with P3HT at a V_{DS} of -1 V (Herlogsson *et al.*, 2007). Despite its poor $I_{\text{ON}}/I_{\text{OFF}}$ ratio and high contact resistance, it had fast switching speed and low voltage operation due to the electrochemical stability of the semiconductor from the large polyanionic chains forming a “barrier” to prevent penetration of the semiconductor. In addition, the presence of protons in the polyelectrolyte backbone may have neutralized any hydroxide ions which may penetrate the semiconductor. The strengths of a single ion-conducting polyelectrolyte were reinforced again in an n-type device, using a polymerized triblock copolymer with a PIL middle block. The ion gel was PS-PIL-PS, where the PIL was [EMIM][TFSI] with the cationic species [EMIM]⁺ polymerized into the backbone of the triblock copolymer for single-ion conduction (Choi *et al.*, 2015). This single-ion conducting gel electrolyte had an ionic conductivity of approximately $1 \times 10^{-3} \text{ mS cm}^{-1}$ and resulted a specific capacitance of approximately $1 \mu\text{F cm}^{-2}$ from displacement current measurements. The attachment of the cationic species to the polymer backbone resulted in limited ionic doping due to the bulky cation chains forming a high charge density EDL at the semiconductor/dielectric interface to enable good n-type electrical performance. The PS-PIL-PS was also hydrophobic and mechanically strong, allowing the deposition of metal electrodes via thermal evaporation and aerosol jet printing of PEDOT:PSS, making it a promising candidate for printed electronics applications. The small hysteresis of the OEGT was also attributed to its single-ion conduction. Nevertheless, the electrochemical doping of ions into n-type semiconductors was found to increase the leakage current significantly, resulting in their irreversible degradation due to charge trapping.

Table 4 shows some of the OEGTs that have been made in the literature using polyelectrolytes and PILs. The architecture often used is again TGBC. The advantages of these electrolytes are their ease of synthesis and solution processability. A major disadvantage for both polyelectrolytes and PILs is their low ionic conductivity, which leads to slow EDL formation and translates to slower switching speed of the OEGT.

Polymer Electrolyte Dielectrics

Polymer electrolytes are ion-coordinating polymer matrices containing mobile ions from dissolved salts in ion-coordinating polymer matrices. Unlike polyelectrolytes or ion gels, these ions are coupled to the polymer backbone. These polymer electrolytes are often cast as gels or films and are often referred to as solid polymer or gel electrolytes. The capacitance provided by polymer electrolytes is in the range of $1\text{--}10 \mu\text{F cm}^{-2}$, while ionic conductivity can be as low as $10^{-4} \text{ mS cm}^{-1}$ and as high as or greater than 10 mS cm^{-1} .

One of the common polymer electrolytes is PEO/LiClO₄. The oxygen lone pairs on PEO coordinate with the Li⁺ to provide coupled ionic motion, so the ionic movement relies on the flexibility of the PEO chain (Kim *et al.*, 2013). The movement of the PEO chain is highly dependent on the glass transition temperature, making it temperature sensitive. In order to improve the movement of the PEO chain, there has been extensive tuning focusing on crosslinking, modification using grafting or copolymerization or blending, and use of additives such as plasticizing agents of nanocomposites. However, these efforts have largely resulted in ionic conductivities of up to only about $10^{-1} \text{ mS cm}^{-1}$.

One promising type of polymer electrolyte which drastically improves the ionic conductivity to the order of $1\text{--}10 \text{ mS cm}^{-1}$ is the composite solid polymer electrolyte (CSPE). Using a blend of PVA polymer matrix, polycarbonate (PC) plasticizer, DMSO solvent, and LiClO₄ salt, the resulting polymer electrolyte has high mechanical strength and stability over a wide range of temperatures and humidity (Marques *et al.*, 2019). The same polymer electrolyte formulation reports an ionic conductivity of up

Table 5 Polymer electrolyte-gated field effect transistors

Dielectric Material	C ($\mu\text{F cm}^{-2}$)	Ionic conductivity (mS cm^{-1})	Configuration	Semiconductor	SD/Gate	V_T (V)	I_{ON}/I_{OFF}	I_{OFF} (A)	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	SS (mVdec^{-1})	V_{DS}
VEGF DNA aptamer, hydrogel, PBS (Pallu <i>et al.</i> , 2019)	N/A	N/A	Probe TGBC	DPP-DTT	Au/Au wire	−0.5	10^3	N/A	N/A	N/A	−0.4
LiClO_4 , PEO (Panzer and Frisbie, 2007)	N/A	N/A	TGTC	P3HT	Au/PEDOT: PSS	N/A	10^5	10^{-8}	3.4	N/A	−1
LiClO_4 , PEO (Panzer, Newman and Frisbie, 2005)	5	N/A	TGBC	Pentacene	Au/Au	N/A	10^4	10^{-10}	0.01	180	−1
H_3PO_4 , PVA (Ton <i>et al.</i> , 2021)	3.2	0.12	In-plane	diF-TES-ADT	Au/Au	−0.7	10^5	10^{-10}	5	91	−0.4

to 5.37 mS cm^{-1} (Von Seggern *et al.*, 2016) and specific capacitance of up to $40 \mu\text{F cm}^{-2}$ (Singaraju *et al.*, 2019). The electrical performance of this CSPE is attributed to its composition which conforms well to the surface of the semiconductor channel, as well as the plasticizer and solvent forming channels for ion travel for improved conductivity and fast EDL formation. In metal oxide semiconductor inorganic OEGTs they have shown good mechanical robustness and compatibility with inkjet printing, forming a fast-drying film on which additional layers of different materials can be printed. However, the compatibility of this particular CSPE with organic semiconductors is unknown. It is possible that the good electrical performance of these OEGTs may not be replicable in organic devices due to the metal oxide semiconductor itself as well as the relative impermeability of sintered metal oxide semiconductor which eliminates issues with electrochemical doping by the CSPE. However, the composition and principle behind the CSPE may still be applied to organic devices.

Another emerging category of polymer electrolytes for OEGTs are proton-conducting polymer electrolytes. Although they have been used in solid state supercapacitors and sensors since the mid-1980s (Polak and Young, 1985) and possess excellent ionic conductivity and capacitance, they have been rarely applied in OEGTs due to environmental instability (same as other polymer electrolytes, ion gels, and polyelectrolytes), and some compatibility issues with other components. One type of proton-conducting polymer electrolyte that may be of interest is a polymer/acid blend such as PVA/ H_2SO_4 or PVA/ H_3PO_4 which have conductivities of up to $10^{-1} \text{ mS cm}^{-1}$. Ton *et al.* have demonstrated the viability of PVA/ H_3PO_4 proton-conducting polymer electrolyte gate dielectrics in organic OEGTs (Ton *et al.*, 2021). In a side-gate device using diF-TES-ADT small molecule semiconductor, they were able to achieve a capacitance of $2.3 \mu\text{F cm}^{-2}$ and ionic conductivity of 0.12 mS cm^{-1} as well as an I_{ON}/I_{OFF} ratio of 10^5 and SS of 91 mV dec^{-1} at a V_{DS} of -0.4 V .

Table 5 summarizes some of the OEGTs that have been made with polymer electrolytes. The architecture is often TGBC. The advantages of these electrolytes are their ease of synthesis, solution processability, and high electrical performance.

OEGT Applications

The rapid growing application of OEGTs include smart textiles, wearables, displays, neuromorphic computing, and biological sensing. The following sections give an overview of the advances and accomplishments in OEGT applications thus far.

Biological Sensing

The most prevalent application for organic OEGTs is biological sensing. In OEGTs, the biorecognition element can be covalently attached to the semiconductor or gate electrode interface through a surface functionalization step. This makes them especially suitable for biosensing as they can perform label-free detection as the biomolecules react with the biorecognition element, resulting in a transduction of a change in physical property such as current, that can be correlated to the biosensing event. However, there are some limitations for OEGT biosensors such as the sensing of only charged biomolecules, low selectivity, and limitations in sensing past the Debye length in some cases.

Most examples of OEGTs in biosensing use a water or salt electrolyte as the gate dielectric. For the most part, the electrolyte used is PBS. This presents another challenge as water-based electrolyte provide little environmental stability and portability. However, they provide highly compatible biological environments.

Examples of biological sensing using organic OEGTs can be found in **Table 6**.

Table 6 Other applications in OEGT biosensing

Analyte	Configuration	Semiconductor	SD/G	Functionalization Location	Dielectric	LOD	Dynamic Range
2,4-D (Nguyen <i>et al.</i> , 2018)	Probe TGBC	DPP-DTT	Au/Au wire	Gate	Water	2.5 fM	10^{-16} – 10^{-13} M
Alpha-fetoprotein (Sun <i>et al.</i> , 2020)	Probe TGBC	PDBT-co-TT ^a	Au/Pt probe	Channel	Water	0.15 ng/mL	1 ng/mL – 1 µg/mL
Biogenic amine (Minamiki <i>et al.</i> , 2018)	In-plane	P3CPT	Au/Au	Channel	Water	1.6 mM	1.6–10 mM
Bisphenol-A (Piro <i>et al.</i> , 2017)	Probe TCBC	pBTTT	Au/Au wire	Channel	PBS	10^{-11} M	1 pM – 1 M
Cortisol (Massey <i>et al.</i> , 2020)	Stacked electrolyte TGBC	TIPS-pentacene ^b	Cr/(PEDOT:PSS, PEDOT:PSS/Graphene)	PMMA layer	PMMA, Teflon, biofilm	27.3 pM	27.3 pM – 27.3 M
C-reactive (Macchia <i>et al.</i> , 2019)	Plate TGBC	P3HT	Au/Au	Gate	Water	210 zM	10^{2-106} zM
Cytokine interleukin-6	Probe TGBC	Pentacene (Diacci <i>et al.</i> , 2017)	Au/Au wire	Gate	PBS	1 pM	1 pM – 10 nM
Dopamine (Casalini <i>et al.</i> , 2013)	Probe TGBC	P3HT	Au/Au wire	Gate	PBS	1 pM	1 pM – 1 mM
Dopamine (Massey <i>et al.</i> , 2019)	Stacked electrolyte TGBC	TIPS-pentacene	Cr/(PEDOT:PSS, PEDOT:PSS/Graphene)	PMMA layer	PMMA, Teflon, biofilm	0.01 M	0.01–1 M
HIV (Sailapu <i>et al.</i> , 2020)	TGBC	P3HT	Au/Au	Gate	PBS	1 fM	N/A
IgG (Macchia <i>et al.</i> , 2018)	Probe TGBC	P3HT	Au/Au	Gate	PBS	20 zM	$6 \times 10^{-2-6.67} \times 10^8$ zM
Influenza A (Poimanova <i>et al.</i> , 2022)	Probe TGBC	BTBT: PS	Au/Pt wire	Channel	PBS	100 nM	N/A
Neurofilament light chain (Solodka <i>et al.</i> , 2022)	Probe TGBC	TIPS-pentacene	Au/Au wire	Gate	PBS	30 fM	100 fM – 10 nM
Odorant binding protein (Mulla <i>et al.</i> , 2015)	Plate TGBC	PBTTT-C14	Au/Au	Gate	Water	50 pM	1–106 pM
Plum pox virus (Berto <i>et al.</i> , 2019)	Probe TGBG	Pentacene	Au/Au	Gate	PBS	180 pg/mL	5 ng/mL–50 µg/mL
Procalcitonin (Seshadri <i>et al.</i> , 2018)	Plate TGBC	P3HT	Au/Au	Channel	PBS	2.2 pM	0.8 pM – 4.7 nM
Ricin (White <i>et al.</i> , 2016)	Floating gate	P3HT ^c	Au/Au	Floating electrode	Ion gel	30 pM	0.3–100 nM
TNF α (Berto <i>et al.</i> , 2018)	Probe TGBG	Pentacene	Au/Au	Gate	PBS	1 pM	$10^{-12-10-9}$
TNF α (Parkula <i>et al.</i> , 2020)	Multigate in-plane	Pentacene ^d	Au/Au	Gate	PBS	3 pM	1 pM – 10 nM

^aResponse time of 2700 s (Sun *et al.*, 2020).^bResponse time of 1×10^{-3} s (Massey *et al.*, 2020).^cSignal-to-noise ratio of 35 ± 7 (White *et al.*, 2016).^dSensitivity of 55 nA dec⁻¹ (Parkula *et al.*, 2020).

Cell monitoring is another biological sensing application that has been used with OEGTs. Table 7 shows the device details for some different transistors that have been used for cell monitoring. No figures of merit were reported, as device performance was assessed based on the transient response of the cells as they were subject to changes in conditions.

Wearables

Solution processability, flexibility, low voltage operation, and large-area manufacturing compatibility also makes OEGTs an appealing option for wearable health care and artificial skin. One area that OEGTs have seen much attention is in pressure sensing. While OTFT pressure sensors suffer from high operating voltage and low sensitivity, organic electrolyte-gated transistors have provided high sensitivity pressure sensing at low operating voltages of less than 1 V. Different from OTFTs which may use PDMS, PMMA, PS, PVF-TrFE, or polyurethane which require extremely thin layers for high gating capacitance, electrolytes can provide very high gating capacitance without such careful control of layer thickness. In addition, their low power operation both fulfills the portable and self-powered requirements for such devices along with the safety considerations which need operating voltages of less than approximately 5 V.

Table 7 Cell monitoring using OEGTs

Analyte	Configuration	Semiconductor	SD/G	Dielectric
Cardiomyocyte (Kyndiah <i>et al.</i> , 2020)	Probe TGBC	diF-TES-ADT/PS	Au/Pt wire	mTeSR
Cyanobacteria (Le Gall <i>et al.</i> , 2020)	Probe TGBC	pDPP-DTT	N/A/Pt	BBM ^a
Neural cells (Cramer <i>et al.</i> , 2013)	Probe TGBC	Pentacene	Au/Pt wire	Liquid
Mesenchymal stem cells (Zhang <i>et al.</i> , 2017)	Dual gate	DPP-DTT	Au/Ag/AgCl	Saline

^aBold's Basal Medium.

Note: Reproduced from Cramer, T., *et al.*, 2013 'Water-gated organic field effect transistors-opportunities for biochemical sensing and extracellular signal transduction'. Journal of Materials Chemistry B, 1 (31) 3728–3741. <https://doi.org/10.1039/c3tb20340a>.

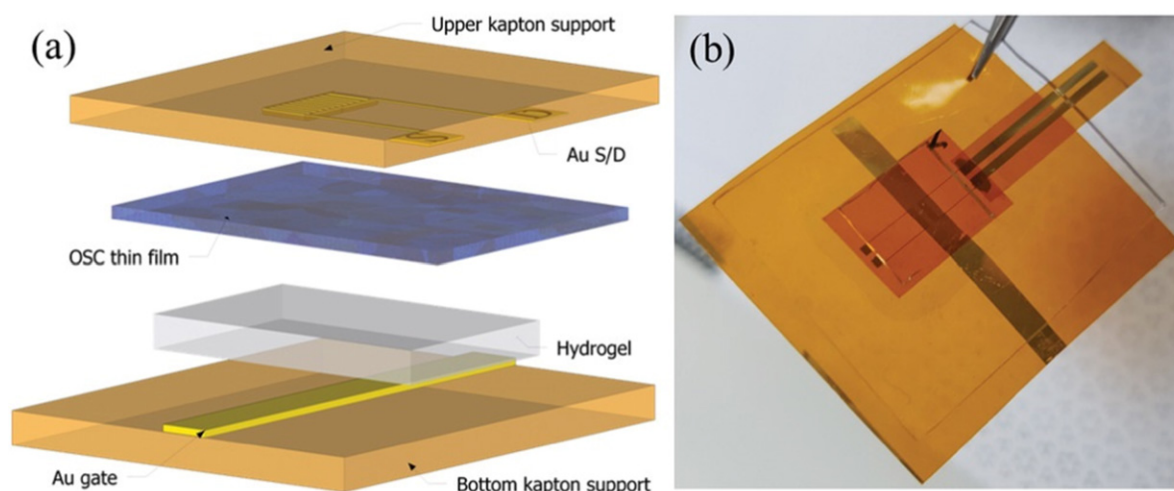


Fig. 10 a) The components used in the hydrogel OEGT and b) the fabricated hydrogel OEGT. Reproduced with permission Zhang, Q., 2019. 'Electrolyte-Gated Organic Field-effect Transistors Based on Organic Semiconductor : Insulating Polymer Blends'. Copyright 2019.

Hydrogels are crosslinked hydrophilic polymers capable of retaining large amounts of water without dissolving. They have been used as effective electrolyte gate dielectrics, providing high capacitance. One issue that OTFTs face is that trace amounts of water in the organic semiconductor from solution processing affect their performance. Zhang *et al.* capitalized on this phenomenon to produce hydrogel OEGT pressure sensors (Zhang, 2019). By using the hydrogel, which provides a constant saturated humidity environment, pressure applied to the device could be correlated to a V_T shift from changes to the water dipole orientation in the semiconductor film. This resulted in devices capable of providing high electrical performance, stability, sensitive low-pressure response (< 10 kPa), and low power consumption. A schematic of the hydrogel OEGT is shown in Fig. 10.

Polyelectrolytes have also been used in pressure sensors. Liu *et al.* developed a polyethylene glycol (PEG) and PAA composite polyelectrolyte used as a gate electrolyte for TCNQ-doped P3HT OEGTs in a suspended semiconductor/dielectric/gate structure (Liu *et al.*, 2019). When pressure is applied on the sensor, the top part of the sensor which is flexible will bend. As such, the semiconductor will make contact with the source and drain electrodes to produce a source-drain current. The sensor has been demonstrated in a wearable 4×4 sensor array suitable for spatial pressure mapping and tactile imaging as well as for future wearable electronics applications. A schematic of the sensor is shown in Fig. 11.

Electrochromic Displays

Transistors are used to control the updating current in actively addressed matrix displays, specifically electrochromic displays. Electrochemical transistors have been used as the control transistor in these applications, but they have slower updating speed and some parasitic features. By replacing the electrochemical transistor with an OTFT, less charge in the semiconductor but faster updating speed and less parasitic features can be achieved. The OEGT can provide additional advantages compared to the OTFT, as they provide high capacitance gating which will lower the operating voltage needed together with the relaxed requirements for very thin dielectric layers. Said *et al.* proposed a design that uses a PSSH common layer as both dielectric in the OEGT and proton transporting layer in the electrochromic display for sub-1 V operation. This will simplify manufacturing for roll-to-roll printing, making it easier to manufacture these large area displays (Said *et al.*, 2009). A schematic of the electrochromic display cell is shown in Fig. 12.

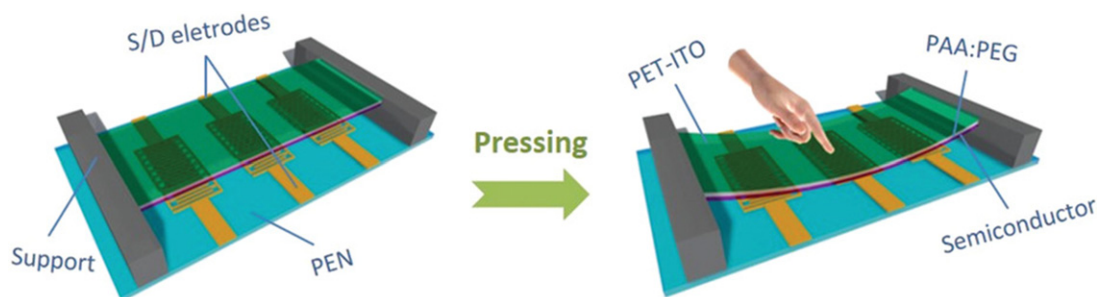


Fig. 11 Schematic showing the suspended semiconductor/dielectric/gate structure of the pressure sensor. Reproduced with permission Liu, Z., *et al.*, 2019. 'Polyelectrolyte dielectrics for flexible low-voltage organic thin-film transistors in highly sensitive pressure sensing'. *Advanced Functional Materials* 29 (1), 1–11. Available at: <https://doi.org/10.1002/adfm.201806092>. Copyright 2019.

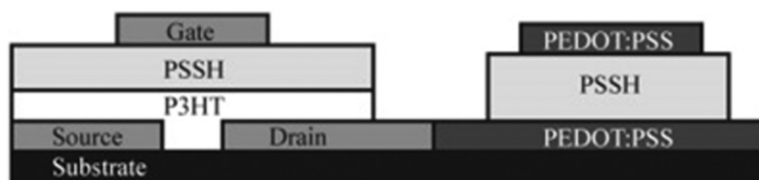


Fig. 12 Structure of the electrochromic display cell with a common PSSH layer. Reproduced with permission Said, E., *et al.*, 2009. 'Electrochromic display cells driven by an electrolyte-gated organic field-effect transistor'. *Organic Electronics* 10 (6), 1195–1199. Available at: <https://doi.org/10.1016/j.orgel.2009.06.008>. Copyright 2009.

Electronic Textiles

Flexible, conductive, and stable textiles are desired for applications in wearable electronics and electronic textiles (e-textiles). Some of the challenges in this field are high manufacturing complexity, high operating voltages, and poor stability from mechanical stress. Electrochemical transistors have been demonstrated as suitable for textile manufacturing with multi-layered assembly (Hamedi *et al.*, 2007; Gualandi *et al.*, 2016), but they operate in depletion mode which limits their applications in logic circuits in addition to a slower switching speed. By using OEGTs, one can avoid depletion mode operation and obtain low operating voltages at high switching speed. Hamedi *et al.* have demonstrated using an ion gel composed of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonimide) ([bmim][Tf2N]) IL in a polymer matrix of poly(1-vinyl-3-methylimidazolium bis(tri-fluoromethanesulfonimide) (poly[ViEtIm][Tf2N]) (Hamedi *et al.*, 2009) to create a woven textile OEGT with a P3HT semiconductor. The fibers were coated with conducting material and polymer semiconductor, then woven and the ion gel was deposited at fiber junctions to form the OEGT as shown in Fig. 13. Interestingly, it has a dual operation mode where initially the current is modulated by a fast field effect, and transitions to slow major bulk electrochemical doping. However, the OEGT retains fast switching speed due to the high ion concentration and fast ion mobility of the ion gel dielectric. Kim *et al.* have also demonstrated a flexible PET textile with embedded gold nanoparticles to create textile OEGTs with stable performance over 1000 bending cycles to create an e-textile suitable for flexible large area textile applications (Kim *et al.*, 2016).

Neuromorphic Computing

OEGTs have another potential opportunity in neuromorphic computing. Currently, digital computation is done based on CMOS technology with von Neumann computer architecture. However, the von Neumann architecture has difficulties in parallel processing (known as the “von Neumann bottleneck problem”) which fail to meet the computational requirements for certain applications such as artificial intelligence or big data analysis. Artificial synapses have been developed to solve this computing issue, by simulating the processing power of the mammalian brain which provides excellent parallel computation where processing and memory are combined. OEGTs are especially promising as artificial synapses as they are flexible, biocompatible, and have ultralow voltage operation due to their gate-channel capacitance operation mechanism (Ling *et al.*, 2020; He *et al.*, 2021; Huang *et al.*, 2021). A biological synapse is depicted in Fig. 14(a). Due to the similar morphology of the OEGT to biological synapses where the gate can represent the pre-synaptic neuron, the electrolyte the synaptic cleft, and the semiconductor the post-synaptic neuron (Huang *et al.*, 2021) as depicted in Fig. 14(b), OEGTs are able to model short term plasticity (STP) in neurons for computation functions.

Lenz *et al.* have demonstrated an advanced organic vertical OEGTs for neural networks. Leveraging a diketopyrrolopyrrole-terthiophene (PDPP) semiconductor and [EMIM][TFSI] IL electrolyte, the OEGT was able to provide an ON/OFF ratio of up to

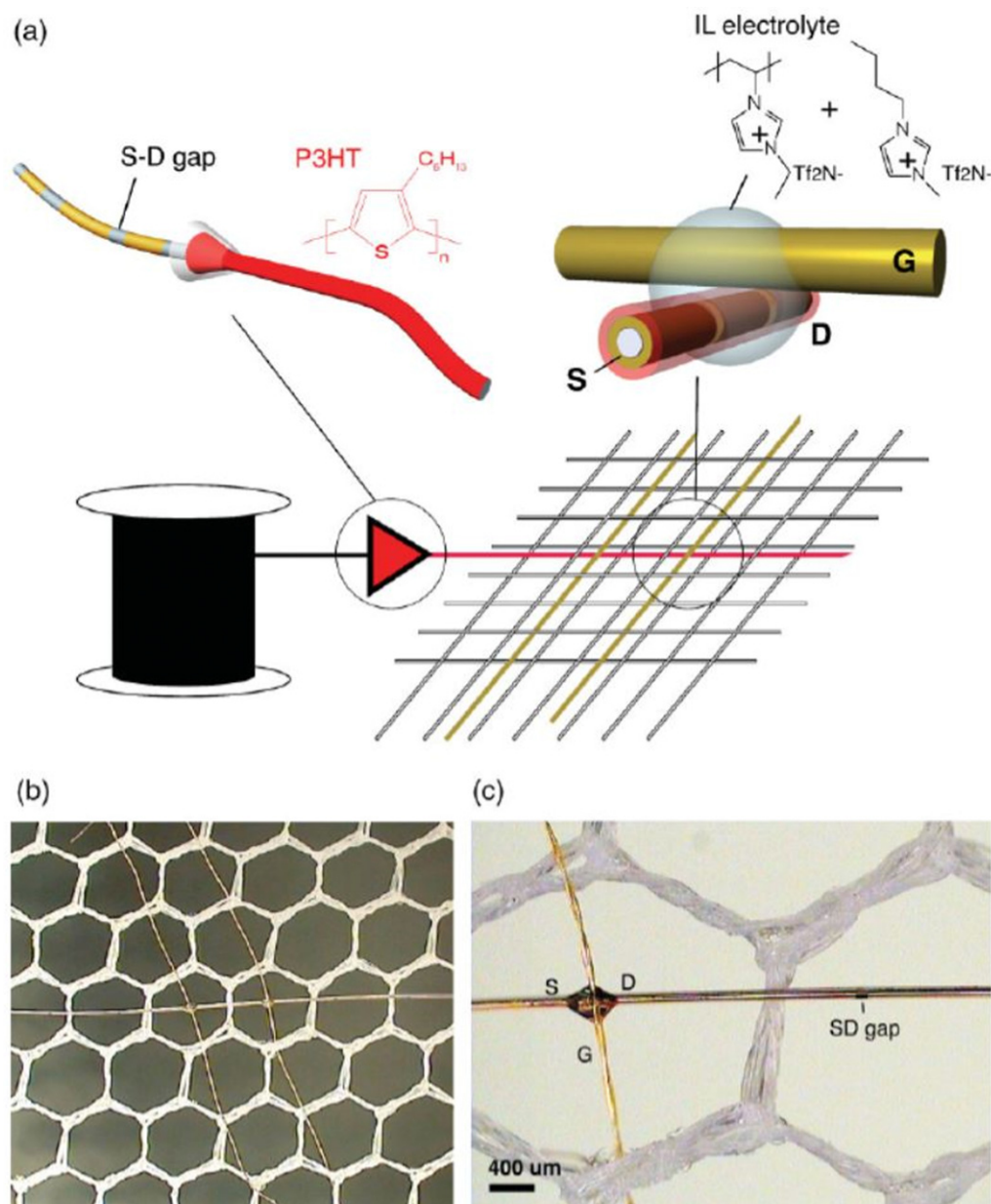


Fig. 13 a) Schematic of P3HT-coated fibres which are woven to form OEGT. The chemical structure of the IL is shown. b) Microscopy image of two transistors created woven into the textile. c) Close up microscopy image of the fabricated transistor woven into the textile. Reproduced with permission Hamed, M., *et al.*, 2009. 'Fiber-embedded electrolyte-gated field-effect transistors for e-Textiles'. *Advanced Materials* 21 (5), 573–577. Available at: <https://doi.org/10.1002/adma.200802681>. Copyright 2009.

10^8 , current density of more than 2 MA cm^{-2} , transconductance of up to 5000 S m^{-1} , and sub-100 fJ energy usage (Lenz *et al.*, 2019). For reference, sub-pJ energy per switching event is required for neural networks (Lenz *et al.*, 2019). The small footprint of the vertical architecture makes this device promising for highly integrated applications. Further work related to this vertical OEGT by Eckel *et al.* has achieved low power operation down to -1 mV with an EMIM:TFSI-based ion gel (Eckel *et al.*, 2022). The fabrication process for this OEGT is shown in Fig. 15.

Additionally, the OEGT as a synapse has also been shown to be biologically compatible. Desbief *et al.* have demonstrated the development of a synapse OEGT using 0.1 M NaCl in deionized water as the electrolyte and pentacene semiconductor with gold nanoparticles at the dielectric/semiconductor interface (Desbief *et al.*, 2016). The synapse was able to demonstrate STP at comparable amplitude of action potential in biological neurons of 50 mV . In addition, stem cells were able to adhere to the surface of the OEGT and differentiate into neurons without strongly affecting the performance of the OEGT synapse.

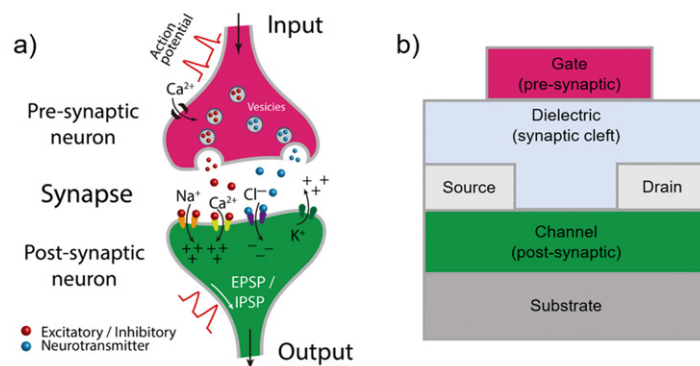


Fig. 14 (a) Schematic of biological synapse. (b) TGTC OECT as an artificial synapse, inspired by Huang *et al.* Reproduced with permission Ling, H., *et al.*, 2020. 'Electrolyte-gated transistors for synaptic electronics, neuromorphic computing, and adaptable biointerfacing'. *Applied Physics Reviews* 7 (1). Available at: <https://doi.org/10.1063/1.5122249>. Copyright 2020. Huang, H., *et al.*, 2021. 'Electrolyte-gated transistors for neuromorphic applications'. *Journal of Semiconductors* 42 (1). Available at: <https://doi.org/10.1088/1674-4926/42/1/013103>.

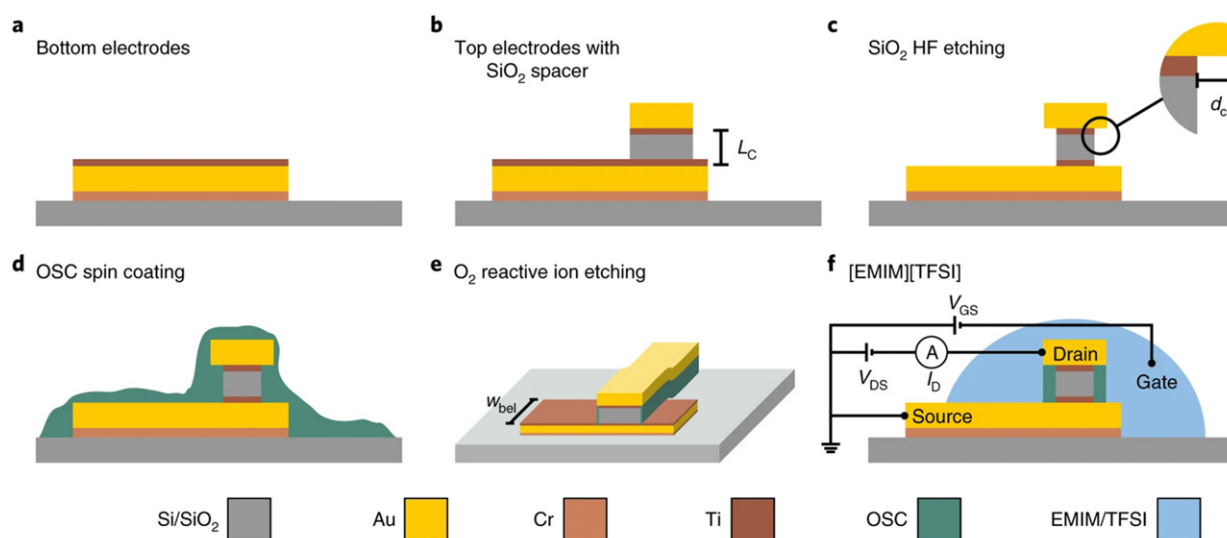


Fig. 15 Fabrication process for vertical organic OEGT for neuromorphic applications. Reproduced with permission Lenz, J., *et al.*, 2019. 'Vertical, electrolyte-gated organic transistors show continuous operation in the MA cm⁻² regime and artificial synaptic behaviour'. *Nature Nanotechnology* 14 (6), 579–585. Available at: <https://doi.org/10.1038/s41565-019-0407-0>. Copyright 2019.

Challenges and Future Opportunities

One of the key advantages of OEGTs is their low voltage operation. This is made possible by the extremely large capacitance of electrolyte gate dielectrics, enabling sub-1 V operation. This low voltage operation as well as ease of integration with other electronic components gives OEGTs an advantage in multiple application areas, such as wearable electronics, tactile sensors, and drivers for electrochromic displays. The solution processability of many OEGTs also makes them compatible with large area and flexible electronics, especially printed electronics.

One area that is especially promising for OEGTs is biological sensing. Since bioreceptors can be functionalized directly onto the gate or channel of OEGTs with aqueous electrolyte, biorecognition events can be transduced into changes in the output current and easily detected by the OEGT. The OEGT can provide current amplification, offering sensitive detection of charged biomolecules at low voltage. While very promising for portable biosensors, there are two main challenges for the OEGT biosensor. One is that the OEGT can only effectively sense charged biomolecules. The other is the dependence on aqueous electrolytes that are not stable in ambient conditions. This limits the usage of OEGTs for portable biosensor devices, such that solid-state electrolytes are required.

Another challenge with OEGTs involves material compatibility. Currently, a majority of OEGTs use gold electrodes that are mostly vacuum deposited and patterned by lithographic processes. Gold is noble and electrochemically compatible with all types of electrolytes in addition to having good conductivity and suitable energy levels for charge injection for p-type semiconductors. However, to capitalize on the large-area, high-throughput and flexible applications for OEGTs towards printed electronics,

solution-processable electrode materials are desired. Although gold ink is commercially available, it is not cost effective. An attractive alternative is silver ink which is much more affordable but known to have undesirable electrochemical reactions with many types of electrolytes. If silver-compatible electrolytes can be developed, there would be opportunities to develop all-printed OEGTs suitable for printed electronics high-throughput fabrication. Graphene-based inks also show potential to replace Au electrodes for printed OEGTs (Singaraju *et al.*, 2019).

The stabilities of OEGTs including electrochemical instability as in the case of silver corrosion, and susceptibility to humidity and temperature are also areas of concern. So far, the addition of additives (Marques *et al.*, 2019), optimization of component composition (Zhang *et al.*, 2016), encapsulation (Alexandrou *et al.*, 2015), physical barriers (Choi *et al.*, 2015), and modification of the transistor geometry (Robin *et al.*, 2019) have been applied to improve the stability of OEGTs, but advances in this area are still required to improve the ambient operation of OEGTs.

The ease of integration of OEGTs in printed circuits has already been demonstrated (Xia *et al.*, 2010; Cadilha Marques *et al.*, 2019), but more emphasis will be focused on the integration of OEGTs into sensing platforms. An opportunity that will come from this is the rise of computer-aided design (CAD). CAD has the potential to significantly reduce the effort and time needed in developing OEGTs. This will be indispensable in guiding efficient experimental work in the future.

Summary

Overall, it has been demonstrated that OEGTs are an important type of OTFT. The use of an electrolyte dielectric is crucial as it provides high gate capacitance for low voltage operation compared to traditional OTFTs. The selection of materials in OEGTs are often flexible and solution processable, making the OEGT promising for all-printed devices and printed electronics. Various electrolytes (aqueous, ionic liquid, ion gel, polyelectrolyte, polymer electrolyte) are compatible with organic semiconductors in many different device architectures to suit a variety of applications. Some of these include wearable sensors, electrochromic displays, e-textiles, neuromorphic computing, and biological sensing. However, the development of compatible OEGT materials is necessary to realize stable, all-printed OEGTs for printed electronics. Further investigation into material compatibility, stability, and computer-aided design will improve the printing, performance, and efficient development of OEGTs for future applications.

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Monolayer Integration of Organic Semiconductors

Shunsuke Yamamoto, Graduate school of Engineering, Tohoku University, Sendai, Japan

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Abstract

This article explains the Langmuir–Blodgett (LB) and related wet processes for the nanoassembly of organic semiconducting materials. After examining the self-assembled monolayer (SAM) and the layer-by-layer (LbL) techniques, the basics and applications of the LB technique, especially those of the nanoassembly of organic semiconducting materials, are overviewed.

Key Points

- Wet processes for the nanoassembly will be surveyed focusing on the layer-by-layer (LbL) and Langmuir–Blodgett (LB) techniques to introduce a wide variety of methodologies for monolayer assembly of organic semiconducting materials.

Introduction

Over the past decade, organic electronics have been developed to realise various commercially available devices such as organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs) (Pope and Swenberg, 1999; Forrest, 2020). A large part of the development was driven by the studies of thin films fabricated by spin-coating or vacuum evaporation techniques. In these films, multiple molecules are connected to the electrode, and the conduction path is spread over a large number of molecules in the bulk region of the film. Consequently, the output characteristics are an ensemble of single-molecule properties. Single molecule-based “molecular electronics” is another branch of organic electronics (Waser, 2012). In this field, precise techniques such as the break junction method or scanning tunneling spectroscopy (STS) are employed to prepare and analyze the single-molecule properties (Reed *et al.*, 1997; Bumm *et al.*, 1996). These methods entail a single molecular contact to the electrode, and the conduction path is a one-dimensional bridge over single or several molecules, which is desirable for fundamental studies on molecular behavior. In between these two fields, “monolayer electronics” is another approach to molecular-sized organic electronics using the advantage of the precise and nanoscale size of molecules. This monolayer approach covers a wide range of dimensionality including the crossover regime from 2-D to bulk 3-D fields using multiple stacking of monolayers. This approach is practical in application fields because monolayer devices have high stability based on multiple molecular junctions and facile fabrication techniques, as described in this article.

Monolayer devices have been developed in conjunction with the evolution of organic semiconducting materials, fabrication techniques, and structural analysis methods. The development of materials and fabrication techniques are two sides of the same coin: it is critical to choose an appropriate fabrication technique depending on the material. In this article, the nanoassembly technique of organic semiconducting materials will be surveyed, focusing on the LB technique, which led to early studies on molecular electronics (Petty, 1996; Pope and Swenberg, 1999), and related wet processes, following the strong connection between molecular structures and fabrication techniques.

Bottom-Up Fabrication Techniques

Bottom-up processes are classified into dry- and wet-state processes based on the fabrication conditions. Atomic layer deposition (ALD) is a typical example of a bottom-up dry process. This technique is performed in a vacuum chamber supplying reactive materials such as aluminum chloride (AlCl_3) and an oxidizing agent alternatively at elevated temperatures (George, 2010). On the other hand, the wet process is completed under mild conditions (occasionally even under ambient conditions) without a vacuum chamber. The SAM technique is a chemical process used to obtain well-ordered layers on substrates. Commonly used reactions for SAM preparations are (1) reactions of thiol (-SH) groups on the gold surface, (2) condensation of silane ($-\text{Si}(\text{OR})_3$) to hydroxyl groups on oxide substrates, and (3) condensation of phosphonic acids ($-\text{PO}(\text{OH})_2$) to metal surfaces. These reactions proceed at room temperature or a elevated temperature depending on the reactivity of the SAM agent (Ulman, 1996; Love *et al.*, 2005). These methods are widely used for passivation of the surface by alkyl chains, such as modifying the gate dielectric in organic field-effect transistor (OFET) devices (Chua *et al.*, 2005; Magliulo *et al.*, 2015; Park *et al.*, 2007). In addition, organic semiconducting materials can be assembled directly using this technique. (Smits *et al.*, 2008) showed the nanoassembly of oligothiophene units using a silane-group-attached molecule. The structure of SAM was investigated using X-ray reflection (XRR) and grazing incidence X-ray diffraction (GIXD) to show that the film is a dense monolayer (Smits *et al.*, 2008). Application to OFETs shows high mobility as high as $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and homogeneous transport through the SAM layer. Novak *et al.* (2011) reported phosphonic acid SAM

with organic semiconducting units to show both p- and n-type operation of OFET devices (Novak *et al.*, 2011). Oligomeric organic semiconductors were also incorporated into the SAM technique to show the advantage of oligomeric SAMs with several π -systems in the backbone which provide a robust function in devices and low sensitivity to π - π mismatches (Gothe *et al.*, 2017).

These examples show the excellence of the SAM-based approach for monolayer assembly of organic semiconducting materials; however, this approach is basically limited to the monolayer assembly of small-molecule and oligomeric materials. The multilayer assembly of polymeric materials is covered by the LbL technique. (Fig. 1) This technique allows multilayer film formation using successive immersions of the substrates into the solutions. Attractive interactions, such as electrostatic interactions, are the driving force of film formation. Decher developed this method for the assembly of conjugated polymers (Decher, 1997). For the LbL deposition of poly(*p*-phenylenevinylene) (PPV), the precursor polymer pre-PPV with a cationic group served as a polycation in LbL cycles and converted PPV during the annealing process after deposition (Lehr *et al.*, 1995). Other conjugated polymers with ionic groups were also incorporated in the LbL technique to afford multilayered films and applied to organic devices such as photo-voltaic devices (Benten *et al.*, 2008). Other interactions, such as complexation and donor-acceptor interactions, are available for the LbL method (Ariga *et al.*, 2014). The complexation-based approach paves the way for the nanoassembly of metal-organic frameworks (MOFs) as thin films and their applications in organic electronic devices. The author and colleagues reported a Cu-

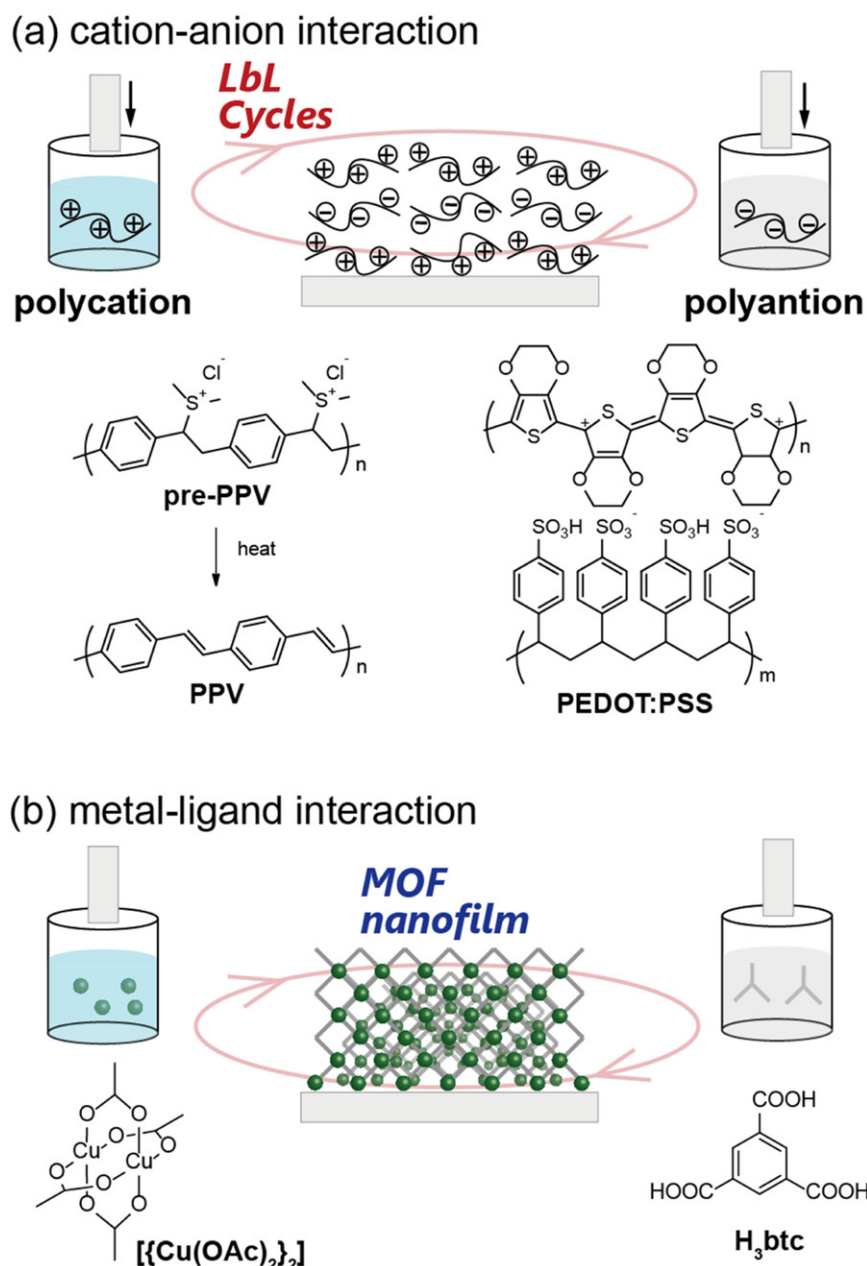


Fig. 1 Schematic illustration of LbL method based on (a) cation-anion interaction and (b) metal-ligand interaction for MOF nanofilms.

based MOF (HKUST-1) thin film fabricated using the LbL method (Ohara *et al.*, 2020). The results show the growth of HKUST-1 as thin films by immersion of polymer-coated substrates into Cu-salt solution and organic linker solution sequentially. The MOF films act as a switching layer for resistive switching in combination with the conjugated polymer PEDOT:PSS. These examples show the high flexibility and controllability of the LbL technique for the fabrication of organic electronic devices, both organic semiconducting and insulating layers.

Overview of the Langmuir–Blodgett Technique

The LB technique is one of the most classic but effective methods for fabricating uniform monolayers in a large area. After the first report by Langmuir and Blodgett, the LB technique has been developed to cover a wide variety of materials, including organic semiconducting materials (Petty, 1996; McCullough and Regen, 2004; Mitsuishi *et al.*, 2006; Ariga, 2020). This technique is based on amphiphilic materials with hydrophilic and hydrophobic moieties. (Fig. 2) These amphiphilic molecules remain on the

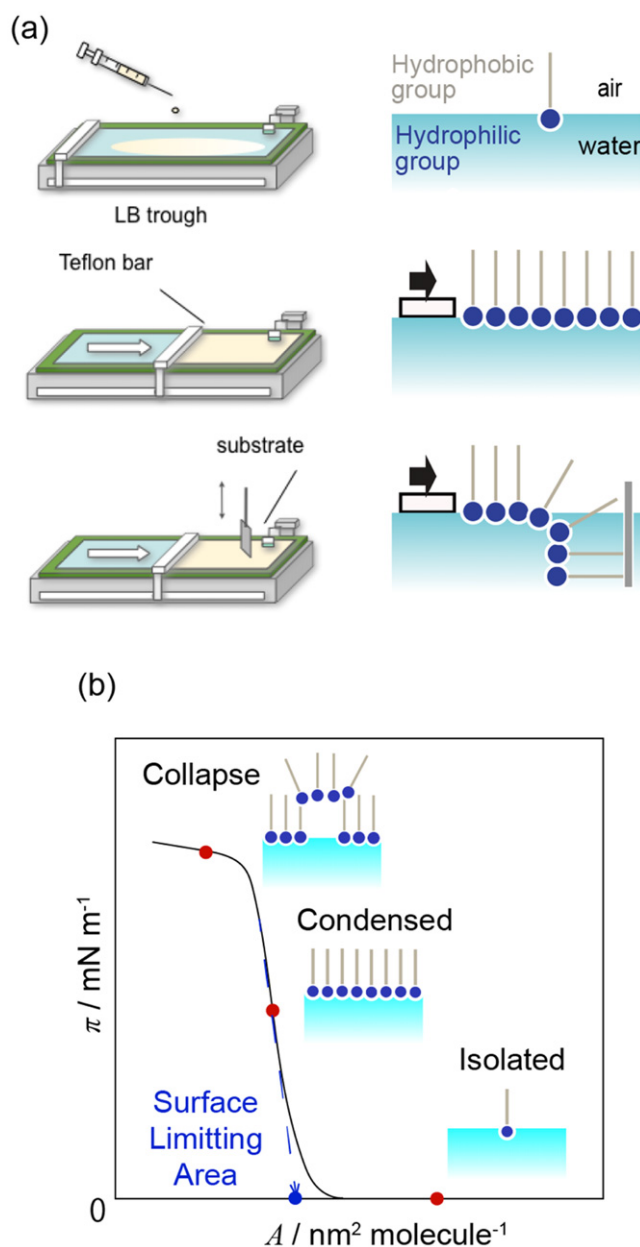


Fig. 2 Schematic illustration of (a) LB method and (b) surface pressure (π) – area (A) isotherm.

air–water interface if the molecule has an appropriate balance between hydrophobicity and hydrophilicity. The balance is estimated by the surface pressure (π) – area (A) isotherm at the Langmuir trough. Here, the surface pressure π is equal to the reduction in surface tension in the presence of a monolayer:

$$\pi = \gamma_0 - \gamma \quad (1)$$

where γ_0 and γ are the surface tensions of the pure subphase and monolayer-covered surface. Important characteristics of the monolayers are their compressibility C_s^{-1} and limiting surface area S , both of which are estimated from π – A isotherms. The compressibility C_s^{-1} is defined in analogy with the bulk compressibility and is obtained from the slope of the π – A isotherm:

$$C_s^{-1} = -A \frac{d\pi}{dA} \quad (2)$$

The C_s^{-1} value is greater in more condensed states, which follows the order, liquid-expanded ($\sim 50 \text{ mN m}^{-1}$), liquid-condensed ($\sim 200 \text{ mN m}^{-1}$), and solid ($\sim 1000 \text{ mN m}^{-1}$) phases (Davies and Rideal, 1963). By combining observations by Brewster angle microscopy (BAM), the phase states can be analyzed more precisely. The limiting surface area S is estimated from a region where the π – A isotherms can be regarded as a linear line in the condensed phase. The intercept of the extrapolated line from the linear region shows the limiting surface area of the molecule. Comparing the projected area of the molecular model and the S value provides information on molecular packing.

The monolayer can be transferred successively onto substrates if the monolayer is sufficiently stable. The monolayer stability is checked using the surface area (A) – time (t) dependency at constant surface pressure. A decrease in the area at a specific pressure indicates the collapse of the monolayer under this condition, which is unsuitable for the transfer process. Both horizontal dipping (Langmuir–Schaefer, LS) and vertical dipping (Langmuir–Blodgett, LB) methods can be used to transfer monolayers. The LS method was used to transfer highly rigid monolayers. The LB method has good compatibility with multiple transfers via a sequential dipping process. The quality of transfer was characterized by the deposition ratio τ , which is the ratio of decreased monolayer area at the air–water interface to the coated area of the solid substrate: τ is 0.95–1.05 in an ideal condition. The deposition modes were classified into X, Y, and Z films, depending on the stacking. The Y-type film is formed via the transfer of a monolayer both at down and up strokes into/from the air–water interface to form symmetric head-to-head and tail-to-tail structures. X (down stroke only) and Z (up stroke only)-type films formed an asymmetric film structure, which are beneficial to the rectifiers and non-linear optical applications.

In the LB technique, amphiphilic materials, including amphiphilic polymers, are required to form a stable Langmuir monolayer. Long alkyl chains are widely used as hydrophobic groups and referred to as “tail” groups. For instance, carboxylic acids, such as stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$) and arachidic acid ($\text{C}_{19}\text{H}_{39}\text{COOH}$) with linear alkyl tails, are classic examples of monolayer-forming molecules. In addition to these small molecules, amphiphilic polymers have also been used in this field. The author and colleagues have investigated the formation and functionalization of polymer LB films consisting of poly(*N*-alkylacrylamide)s. Poly(*N*-dodecylacrylamide) (pDDA) exhibits excellent LB film formation ability to provide highly oriented and densely packed monolayers at the air–water interface. The transfer of pDDA monolayers proceeds at a high surface pressure of approximately 30 mN m^{-1} , affording a Y-type film with more than 100 layers (Miyashita *et al.*, 1989, 1990, 1994). These excellent properties are based on the network of hydrogen bonds among hydrophilic amide groups at the air–water interface. Copolymerization is an effective strategy for the functionalization of materials. For example, we reported a pDDA-based copolymer functionalized with catechol groups, which are used in adhesive biofunctional materials, including adhesive proteins of marine mussels (Waite and Tanzer, 1981; Lee *et al.*, 2007). Catechol-based copolymers form stable monolayers and are deposited on solid substrates with nearly unity transfer ratios in Y-type films. The adhesion of oxide nanoparticles (SiO_2 , Al_2O_3 , and WO_3) was demonstrated to show pH-dependent deposition of nanoparticles corresponding to the catechol–quinone transition in p(DDA/DMA) films. This technique has the potential for the fabrication of nanoparticle-based devices (Yamamoto *et al.*, 2016). As outlined here, both monomeric and polymeric amphiphilic materials have been developed and applied to the nanoassembly of organic semiconducting and organic-inorganic hybrid devices.

Nanoassembly of Organic Semiconducting Materials by Langmuir-Blodgett Technique

An application of the Langmuir–Blodgett technique is the nanoassembly of organic semiconducting materials. Organic semiconducting materials are composed of aromatic groups with π -electrons for their optoelectronic properties. This indicates that these materials are essentially hydrophobic. For LB nanoassembly, there are several strategies to provide amphiphilic properties (Fig. 3). Nakahara *et al.* (1987) systematically investigated the LB assembly of oligothiophenes with various hydrophilic groups. They reported that a terthiophene with an ester group (1 in Fig. 3) formed a stable monolayer and uniform Y-type transfer on solid substrates. The deposited LB films showed high conductivity, which was enhanced by halogen doping. They also investigated a mixed-monolayer approach to achieve stable monolayer formation of oligothiophenes (5 and 6 mer) with the aid of arachidic acid ($\text{C}_{19}\text{H}_{39}\text{COOH}$). This study clearly shows two strategies for the nanoassembly of organic semiconducting units: (1) the use of organic semiconducting material with polar groups and (2) mixing a stabilizing agent in hydrophobic molecules. After these studies in the 1980s, the LB nanoassembly techniques were developed based on these strategies to achieve precise structural analysis and application to organic semiconducting devices. For example, Metzger *et al.* reported an LB-based diode device using the zwitterionic molecule (2) (Metzger, 1997). This molecule has π -conjugated and ionic parts, which serve as an electronic and hydrophilic group with a long alkyl chain,

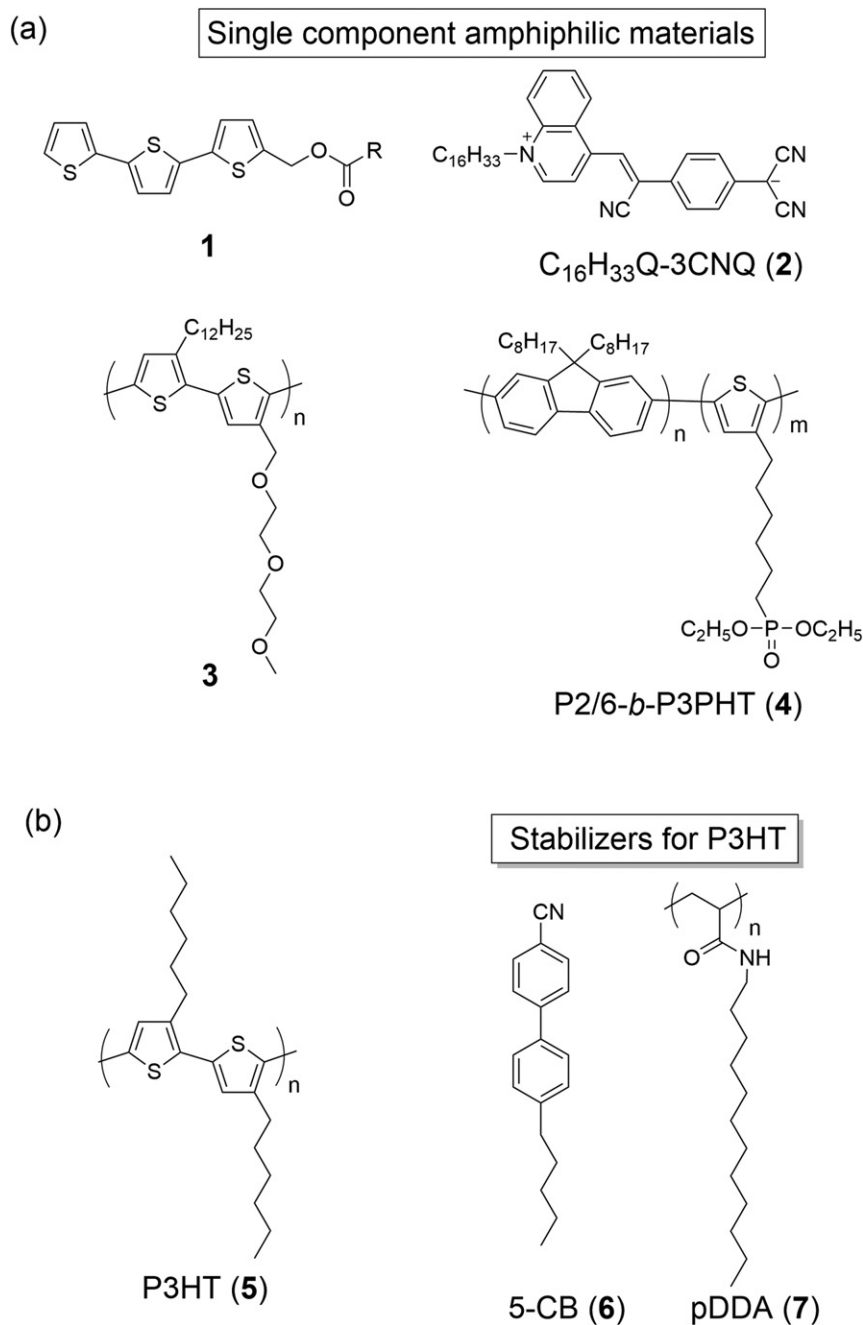


Fig. 3 Chemical structures of (a) single component amphiphilic polymer materials and (b) stabilizers for P3HT used in the LB method.

which serves as a hydrophobic group in one molecule. The monolayer was transferred as a Z-type film with an asymmetric film structure, which is the origin of diode operation. The rectifying property followed the Aviram-Ratner model based on electron transfer from the donor to acceptor moieties (Aviram and Ratner, 1974). These LB-based devices, including OFET (Paloheimo *et al.*, 1990) reported in the early 1990s, proved the excellence of the LB technique in organic electronics.

In addition to the small molecular amphiphiles mentioned above, amphiphilic polymers have also been introduced in this field. Bjørnholm *et al.* designed a series of polythiophenes with both hydrophilic and hydrophobic side chains (3) (Reitzel *et al.*, 2000). Polymers with long alkyl and oligo ethylene glycol chains form monolayers with high stability at the air–water interface, whereas polymers with only hydrophobic side chains do not form monolayers. In the monolayer of the amphiphilic polymer, the thiophene ring is oriented normal to the water surface in the monolayer from GIXD measurements at the air–water interface. A detailed analysis shows that the regioregularity primarily affects the stability and structure of the monolayers. This study shows that side chain engineering is an effective approach for the LB nanoassembly of organic semiconducting polymers. Scherf and Advincula *et al.* reported a block copolymer (4)

composed of polyfluorene with hydrophobic side chains and polythiophene with hydrophilic side chains (Park *et al.*, 2008). This study demonstrates that the block copolymer monolayer shows various 2-D phase states depending on the surface pressure at the air–water interface. The backbones of the thiophene rings adopt an edge-on arrangement similar to the work of Bjørnholm, as mentioned above. These examples show that the proper design and arrangement of hydrophobic moieties is the key to LB nanoassembly using amphiphilic polymers.

Another approach is to use amphiphilic non-conjugated “white” materials as a stabilizing agent for the monolayer. In early studies, fatty acids such as stearic acid (Skotheim *et al.*, 1989) and arachidic acid (Paloheimo *et al.*, 1990) were reported to serve as stabilizers for poly(3-hexylthiophene) (P3HT, 5) LB films. After these studies, Nagano *et al.* (2008) employed a liquid crystal molecule, 4'-pentyl-4-cyanobiphenyl (5CB, 6), as a stabilizing agent for the P3HT monolayer. Analysis of the π -A isotherm demonstrated that the addition of 5CB enhanced the stability of the monolayer. These two components were homogeneously mixed without significant phase separation, and the hybrid monolayers were transferred on a solid substrate with a transfer ratio of unity. Furthermore, 5CB was removed by annealing after deposition. The combination of 5CB removal and horizontal dipping (LS method) affords multilayer P3HT films. The deposited P3HT films were applied to the channel layers of the OFET device to show a percolative charge transport network in the 2-D plane. The device property shows nonlinear behavior that was explained by the Coulomb blockade mechanism (Akai-Kasaya *et al.*, 2015). This example demonstrates the effectiveness of liquid crystal molecules as stabilizing agents. In addition to small molecules, amphiphilic polymers also serve as stabilizing agents. Matsui *et al.* (2005, 2007) reported the use of a mixed monolayer of P3HT and pDDA (7) as stabilizing agents. A mixed solution of these polymers (typically, P3HT:pDDA = 2:1) was spread on the air–water interface and transferred onto solid substrates by vertical dipping to afford Y-type films. The absorbance of the deposited films increased linearly on the deposition cycle up to 20 layers, indicating uniform multilayer deposition. The film structure was investigated to show that P3HT forms domains on top of the pDDA by squeezing out from the air–water interface and depositing onto the solid substrate. The mixed monolayers were applied to the channel layer of both OFET (SiO₂-gated) and OEET (electrolyte-gated) devices to show clear enhancement-mode operations. This example shows the excellence of amphiphilic polymers as stabilizers for conjugated polymer materials (Fig. 4).

The “third” approach is the hybrid of the two strategies mentioned above: designing amphiphilic semiconducting molecule and blending it with the stabilizer. This approach has the potential to cover a wide range of π -conjugated units in monolayers to cover the crossover regime from 1-D to 3-D systems by tuning fabrication parameters such as the mixing ratio of the stabilizer and layer numbers. The author and colleague propose a versatile and facile low-dimensional integration approach with π -conjugated units using newly designed acrylamide-based polymers and π -conjugated units in the side chains. A homopolymer poly(9-ethyl-3-carbazolyl acrylamide)

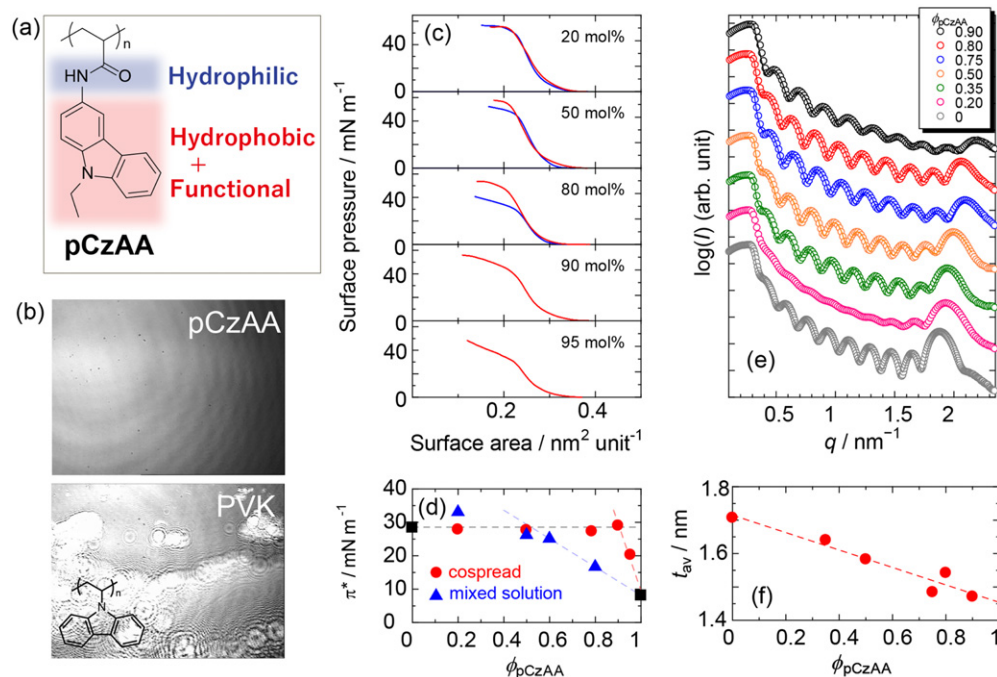


Fig. 4 (a) Chemical structure of pCzAA. (b) BAM images ($400 \times 300 \mu\text{m}^2$) of pCzAA and PKV monolayers on Langmuir trough. (c) π -A isotherms of pCzAA:pDDA monolayers measured at 20°C: co-spreading (red) and mixed solution spreading (blue). (d) Plots of π^* as a function of pCzAA contents: co-spreading (red) and mixed solution spreading (blue). Black symbols correspond to single component spreading. (e) X-ray reflectometry profiles of pCzAA:pDDA nanosheets (20 layers) from co-spreading method. Solid lines show fittings using box model. (f) Average monolayer thickness calculated from the fittings. Reprinted (adapted) with permission from Yamamoto, S., Nishina, N., Matsui, J., Miyashita, T., Mitsuishi, M., 2018. High-density and monolayer-level integration of π -conjugated units: Amphiphilic carbazole homopolymer Langmuir–Blodgett films. *Langmuir* 34, 10491–10497. Copyright (2018) American Chemical Society.

(pCzAA) was designed based on the structure of pDDA and the monolayer behavior of the amphiphilic polymer pCzAA was investigated by comparing it with the hydrophobic polymer poly(*N*-vinylcarbazole) (PVK) (Yamamoto *et al.*, 2018). The π -A isotherms indicated that pCzAA forms a monolayer at the air–water interface and that the hydrophilic amide group plays a key role in monolayer formation, in contrast to the random aggregation of PVK at the air–water interface. Although pCzAA forms a stable monolayer, the transfer ratio of the monolayer was approximately 0.6, without the blending of a stabilizing agent. For the uniform transfer of monolayers, pCzAA:pDDA blend monolayers were formed using two methods: (1) spreading mixed solution of pCzAA and pDDA (mixed solution method) and (2) spreading each solution separately (co-spreading method). As a result of pDDA addition, even a small amount of pDDA stabilized the pCzAA monolayer. The π^* value, at which the compressibility modulus C_s^{-1} reached a maximum, drastically increased upon the addition of 10 mol% of pDDA. This behavior depends on the blending method; 40 mol% addition of pDDA is required to stabilize pCzAA:pDDA monolayers using the mixed solution spreading method. This indicates that the phase-separated structure in the Langmuir film is a key factor in monolayer stabilization by pDDA. The high pCzAA content exceeded that of the percolation threshold in the 2-D plane (45 mol%), (Kirkpatrick, 1973) indicating the formation of the charge transport pathway in the in-plane direction. The area per monomer unit for pCzAA S_{Cz} is independent of the pCzAA content from 50 to 90 mol% pCzAA at approximately $0.28 \text{ nm}^2 \text{ unit}^{-1}$, corresponding to the projected area of the carbazole groups in edge-on orientation. The pCzAA:pDDA co-spread monolayers were transferred onto hydrophobic substrates for both the up-stroke and down-stroke, indicating Y-type film deposition. AFM images of the nanosheets showed a phase-separated structure with disk-like domains 100–500 nm in diameter by the co-spreading method, indicating that the pCzAA:pDDA monolayers undergo phase separation. The transferred films formed a highly ordered layered structure in the out-of-plane direction, as confirmed by the XRR measurements. The co-spreading of amphiphilic carbazole homopolymers is effective for hydrogen bond formation with large-scale phase-separated structures to enhance the monolayer stability and transfer ability. Remarkably, the deposited film showed high heat resistivity upon annealing at 150°C in vacuum. The XRR and AFM measurements indicated that the layered structure of pCzAA:pDDA films was maintained during thermal annealing with minor relaxation in the structure. This means that the polymeric approach can fabricate stable organic electronic devices, which is a challenging issue for small-molecular-based LB film devices. The author and colleagues are now studying the nanoassembly of multiple kinds of organic semiconducting moieties, such as bithiophene, to investigate the versatility of this approach. This example shows the possibility of controlling the dimensionality of π -conjugated nanoassemblies using the LB technique with acrylamide-based polymers having π -conjugated units. The LbL and LB techniques are compatible with polar (or aqueous) environments; hence, nano-integration of biomolecules can be achieved using these methods for organic electronics, especially sensor applications. Organic-mixed conducting materials (Paulsen *et al.*, 2019; Rivnay *et al.*, 2018), which conduct both ions and electrons (holes), is another promising field for LB and LbL nanoassembly using polar (hydrophilic or ionic) moieties as ion transporting groups.

Summary

In this article, several wet processes for the nanoassembly of organic semiconducting materials are described. The SAM method is used for monomeric materials with reactive groups such as thiol, silane, and phosphonic acids. Polymeric materials with ionic groups can be assembled using the LbL methNuzzood, which has high flexibility in terms of materials and deposition methods. The LB technique can produce highly ordered films with multilayered structures. LB-compatible materials can be prepared using a single component of designed semiconducting materials and/or by blending stabilizing agents with organic semiconducting materials. Among these techniques, it is crucial to choose the appropriate method according to the chemical structure of the material. These nanoscale fabrication techniques will pave the way for developing organic electronics, bringing out the potential of the materials.

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Organic Light-Emitting Diodes

Guohua Xie, The Institute of Flexible Electronics (Future Technologies), Xiamen University, Xiamen, PR China
Qin Xue, Department of Physical Science and Technology, Central China Normal University, Wuhan, PR China

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Abstract

Based on organic semiconductors, organic light-emitting diodes (OLEDs) as surface light sources are attracting global interest due to their merits of light weight, fast response, excellent flexibility, and high efficiency. This article discusses the developments of OLED materials and device structures. Fundamentals of device physics, fabrication, and characterization have been elaborated. In addition, versatile applications of OLEDs in displays, lighting, photodynamic therapy, and visible light communication are briefly illustrated to guide the readers to better understand the cutting-edge technology.

Nomenclature

e	elementary charge (C)
V	voltage (V)
J	current (A)
k_B	Boltzmann's constant (J/K)
T	temperature (K)
σ	conductivity (S/m)
β	electrical dependent constant ($m^{1/2}/V^{1/2}$)
μ	mobility (cm^2/Vs)
d	device thickness (nm)
E	electrical field (V/m)
ε	dielectric constant
ε_0	permittivity in free space (F/m)
kr	radiative recombination rate (s^{-1})
k_{nr}	non-radiative recombination rate (s^{-1})
τ	exciton lifetime (s)
Φ	photoluminescent quantum yield
γ	charge balance factor
η_{EQE}	external quantum efficiency
η_r	radiative recombination ratio
η_{oc}	light out-coupling efficiency
I_e	radiant intensity (C)
N_e	number of the injected electrons
N_p	number of the emitted photons
$I(\lambda, \Omega)$	spectral radiant intensity (W/nm/sr)
Ω	solid angle (rad)
θ	polar coordinate (rad)
φ	polar coordinate (rad)
λ	wavelength (nm)
h	Planck's constant ($J \cdot s$)
L	luminance (cd/m^2)
c	speed of light in vacuum (m/s)
$V(\lambda)$	photonic efficiency function of human eye
A	area (m^2)

Key Points

- Introduction of the principle and applications of organic light-emitting diodes (OLEDs) for general readers who have no knowledge of this topic.
- Providing the guidance to the early career researchers who aim to explore OLEDs.
- Suggestions on the directions for senior researchers from different research areas/backgrounds to start the interdisciplinary collaborations on OLEDs.

- Tips for the industrial investors to better understand the past, present, and future of OLEDs, which would be helpful for them to make decisions.

Introduction

Organic electronics is one of the emerging subjects which involve technological innovation and change the life of human being. In this article, one of the most important issues of organic electronics, i.e., organic light-emitting diodes (OLEDs) which convert electricity into light, is introduced and elaborated, including the history of organic electroluminescence, the luminescent mechanisms, the practical applications, and future developing directions.

Electroluminescence and Development of OLEDs

Electroluminescence

The conversion of the electricity into photon/light is generally called electroluminescence (EL), which was first observed by Henry and Round in 1907 and documented in an academic report by Destriau in 1936 (Karsnov, 2003; Destriau, 1960). The electrical field, induced by either direct current (DC) or alternating current (AC), plays the vital roles in the EL processes, which become ubiquitous in our daily lives nowadays. An EL device typically consists of two electrodes and at least a layer of the luminescent substance. Vlasenko and Popkov demonstrated the first EL devices with the thin-film architecture in 1950s.

In fact, the first light-emitting diode (LED) with a p-n junction was demonstrated by Losev in 1927 (Lossev, 2009). Initially, the EL from LEDs could only produce infrared, red, and green colors with poor efficiencies and low brightness. In 1993, Nakamura fabricated and demonstrated high-brightness blue LEDs based on gallium nitride (GaN) with the emission peaks at 410–420 nm, which led to the commercial use (Nakamura *et al.*, 1993). Now the colors produced by the EL processes can be easily achieved by the bandgap engineering of semiconductors where photons are generated by radiative recombination.

Development of OLEDs

Similar to LED based on inorganic semiconductors, organic LEDs (OLEDs) are composed of the stacks of different functional layers. As shown in Fig. 1 (a) typical OLED possess an anode, an emitting layer (EML), a cathode, assisted by hole injecting layer (HIL), hole transporting layer (HTL), electron transporting layer (ETL), and electron injecting layer (EIL) which will be grown on a substrate in order once needed. In most cases, the total thickness of the organic layers in OLED will be about 100 nm-scale. Each layer could be individually tuned to manipulate the overall performances. For instance, no HIL is required if the HTL has a good energy level alignment with the anode and the thickness of the HTL could be varied in the range of several hundred nm to maximum the light outcoupling efficiency. Unlike inorganic LEDs, most of OLEDs have no clear p-n junctions.

In the early 1950s, the EL from organic compounds driven by AC current was firstly reported By Bermanose *et al.* (1953). Pope demonstrated the DC (400 V) driven EL of a 10–20 μm -thick anthracene crystal with the modified ohmic contact in 1963 (Pope *et al.*, 1963). The EL from polymer was reported by Partridge who designed a double-layer device architecture composed of polyvinylcarbazole/anitimony pentachloride in 1982 (Partridge, 1983). Attributed to the low work function cathode of cesium, charge carriers could be injected into the luminescent polymer, which resulted in the visible blue emission in room light condition. The current density at 10 V ranged from 10^{-3} to 1 A/m^2 when the thickness of polyvinylcarbazole varied from ca. 5–0.4 μm , correspondingly.

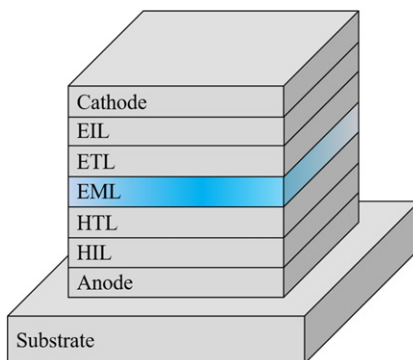


Fig. 1 A typical device stack of OLED.

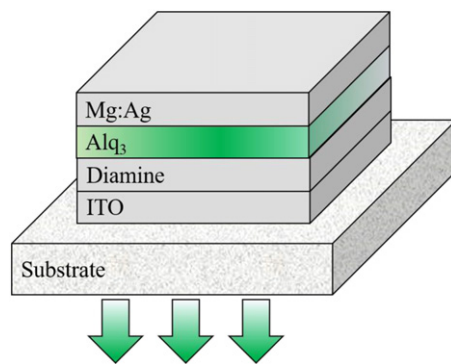


Fig. 2 Device architecture designed by Tang. Reproduced from Tang, C.W., VanSlyke, S.A., 1987. 'Organic electroluminescent diodes'. *Applied Physics Letters* 51 (12), 913–915.

The first bright ($> 1000 \text{ cd/m}^2$) and efficient OLED driven by low DC voltage ($< 10 \text{ V}$) was demonstrated with an external quantum efficiency (EQE) of ca. 1% by Tang at Eastman Kodak in 1987 (Tang and VanSlyke, 1987). As shown in Fig. 2, this device consisted of the HTL Diamine, the ETL 8-hydroxyquinoline aluminum (Alq_3), the transparent anode indium-tin-oxide (ITO), and the low work-function composite cathode (Mg:Ag). The thickness of the ETL was as thin as 60 nm, which resulted in the visible green emission (peaking at 550 nm) at a low driving voltage down to 2.5 V. Although the device lost 30% light output with 10 h at an initial luminance of ca. 50 cd/m^2 , this work pioneered the research in thin-film based OLEDs towards practical applications.

Burroughes from Cavendish Laboratory at Cambridge University employed a luminescent polymer poly(*p*-phenylene vinylene) (PPV) as the neat EML with a thickness of ca. 100 nm spin-coated on the ITO substrate, published in 1990 (Burroughes *et al.*, 1990). The polymer-based OLED achieved a maximum EQE of 0.05%. Due to the high injection barriers of charge carriers with such a simple device architecture of ITO/PPV/Al, the threshold was as high as 14 V and the electrical field across the devices was about 10^6 V/cm which looked common regardless of thin-film or crystal-based OLEDs in order to trigger the EL phenomena. This work paved the way towards solution-processed OLEDs.

The first multilayer white OLED was reported by Kido in 1995 (Kido *et al.*, 1995). By deliberately allocating the red/green/blue emissive zones in different layers (see Fig. 3), the device exhibited a luminance of 2200 cd/m^2 at 16 V and broad spectrum in the visible region peaking at 600, 520, and 410 nm, corresponding to the EL from Nile Red, Alq_3 , and TPD, respectively. In addition, the maximum power efficiency (PE) was about 0.5 lm/W at a luminance of 300 cd/m^2 . This work inspired the research of white OLEDs for solid-state lighting.

In 1998, two independent groups reported the EL originated from the triplet excitons of the heavy-metal complexes, which was regarded as phosphorescence (Baldo *et al.*, 1998; Ma *et al.*, 1998). Baldo *et al.* introduced a platinum complex (PtOEP) as the emissive dopant diluted in the host compound Alq_3 , which produced a maximum EQE of 4% of the thermally evaporated phosphorescent OLED (PhOLED) (Baldo *et al.*, 1998). Two lead investigators involved in this work, i.e., Prof. Forrest and Prof. Thompson, collaborated closely with the company Universal Display Corporation (UDC) to accelerate the commercialization of phosphorescent emitters which play an important role in OLED markets today. The other pioneering research of PhOLED was conducted by Ma who synthesized several Osmium(II) complexes and demonstrated the solution-processed OLEDs with a structure of ITO/PVK:Os(II)/PBD/Al, where PVK denoted as poly(*N*-vinyl carbazole) and PBD was short for 2-(4-biphenyl) – 5-(4-*tert*-butyl-phenyl) – 1,3,4-oxadiazole (Ma *et al.*, 1998). The phosphorescent EL originated from triplet metal-ligand charge-transfer suggested the prospective strategies to maximize the device performances via triplet excitons who were non-radiative in the conventional fluorescent emitters without spin-orbital coupling induced by heavy metal atoms.

In 2009, Adachi's group initially explored the reverse intersystem crossing (RISC) of the Sn^{4+} -porphyrin complexes and confirmed that the triplet-to-singlet up-conversion was easily accelerated by thermal activated, in the presence of a small singlet-triplet gap (ΔE_{st}). Most importantly, the delayed fluorescence components were amplified when the temperature increased, i.e., thermally activated delayed fluorescence (TADF) (Endo *et al.*, 2009). Later, purely organic compounds were successfully synthesized and demonstrated as TADF emitters to deliver nearly unity internal quantum efficiencies and highly efficient devices with almost 100% exciton utilization ratios, which led a new wave of molecular innovation for more cost-effective OLEDs (Uoyama *et al.*, 2012).

Chasing the unity exciton utilization becomes an endless topic in OLEDs. In 2014, Ma proposed a new route to harvest the triplet excitons via hybridized local and charge-transfer excited state (HLCT), where RISC tended to be more efficient via high-lying charge-transfer states since the ΔE_{st} is small enough (Li *et al.*, 2013). Back to 2015, Li's group synthesized a deep-red neutral π radical emitters, which allowed the transition between the lowest singly unoccupied molecular orbital (SUMO) and the highest singly occupied molecular orbital (SOMO), i.e., radiative doublet excitons (Peng *et al.*, 2015). This work inspires a totally new strategy to search the emitters for OLEDs beyond the importunate triplet issues. Challenge and opportunity are coexisting in the future development of OLEDs.

Commercialization of OLEDs

The unique properties of flexibility, light weight, large area, and ease of fabrication make OLEDs very competitive and fashionable for displays and solid-state lighting. In 1997, Tohoku Pioneer started to mass produce OLED displays, targeting for cell phones and

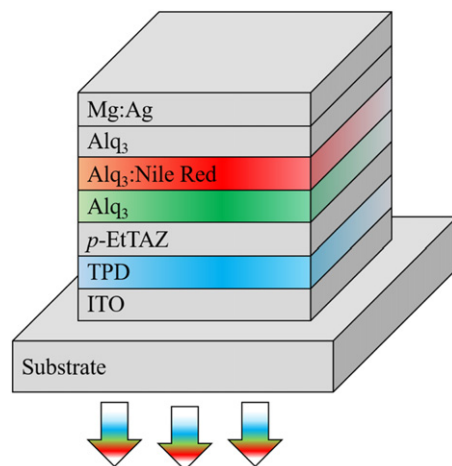


Fig. 3 White device architecture reported by Kido. Reproduced from Kido, J., Kimura, M., Nagai, K., 1995. 'Multilayer white light-emitting organic electroluminescent device'. *Science* 267 (5202), 1332–1334.

in-car audio systems (Pioneer, 2021). Eastman Kodak and Sanyo collaborated each other to start producing OLED displays since 1999. Soon, they demonstrated the world's first display with the active matrix OLEDs (AMOLEDs) (Hara, 2001). Began with the passive matrix OLEDs (PMOLEDs) in 2001, Samsung Display is now devoted to small- and medium-size AMOLED displays, such as smart phones and laptops, and currently it occupies most of the market share of OLED displays (Samsung, 2021).

In October 2007, the Japanese company Sony announced the world's first OLED TV (XEL-1) which was only 3 mm-thick and featured a high contrast ratio of 1000,000:1 (OLED-info, 2017). Due to the low yield and high price, the large-size OLED displays develop very slowly. Found in 2015, JOLED quickly started a pilot line in 2016 and then mass-produced the printed OLED displays for medical monitors in 2017 (JOLED, 2021). Owing to the long-term investment and technologic innovation, the Korean company LG Display set up a G8 OLED TV pilot line in Paju in 2014 and G8.5 OLED TV pilot line in Guangzhou in 2019 (LG, 2021). Now, it becomes to only supplier of large-size OLED TVs, covering flexible, rollable, and transparent series.

OLEDs are capable of covering full sizes of the displays. Unlike the cell phones and TVs, the pixel sizes of microdisplays could be sufficiently smaller than tens of micrometers, typically 5 ~ 30 μm and the diagonal size is less than 1 in.. As an emerging near-eye display technology, OLED microdisplays could offer the ultra-high resolution and the extremely augmented screen, combined with the embedded optical elements. This makes them popular in augmented reality (AR) and virtual reality (VR) for entertainment and interactive products, and head-mounted displays for military applications. The American company, eMagin, started to commercialize SVGA+ (> 800 × 600) AMOLED microdisplays since 2001 (eMagin corporation, 2021). Besides, MicroEmissive Displays (MED), Fraunhofer FEP in Dresden, and MicroOLED based in France were also aiming to commercialize OLED microdisplays (Fraunhofer, 2021; Microoled, 2021).

In recent years, China has invested intensively in OLED industry due to the appealing consumer markets (OLED-info, 2021). Globally, it was reported in May 2021 that the penetration rate of OLEDs in the smartphone market reached 50% and thus surpassed LCD in 2022 (Kimeery, 2021). Attributed to the high display quality, the free-from design, and the reduced prices, OLED displays are flourishing although the strong competitors are appearing, e.g., micro-LEDs based on inorganic semiconductors.

In the field of lighting, OLEDs are expected to be more human-friendly due to the reduced hazardous deep-blue light in the range of 410 ~ 430 nm. The Japanese company, Lumiotec, was the world's first company to develop, produce and sale OLED lighting panels (Lumiotec, 2021). Later, the leading lighting makers, including, Philips, OSRAM, GE, Konica Minolta and Panasonic joined the competition of advocating and developing OLED lighting panels. Based in US and Germany, OLEDWorks is now advancing multi-stack OLED technology for lighting panels after inheriting from Kodak's business in 2010 (Gardner, 2019). Yiguang, based in China is capable of volume production OLED panels for lighting and automotive tail lamps (see Fig. 4) (Yiguang, 2021).

Beyond displays and solid-state lighting, there are many more applications of OLEDs, such as sensing, medical treatment, and visible light communications are currently under development.

Charge Carriers and Excitons

Charge Carriers

Under positive bias, holes and electrons are injected respectively from the anode and the cathodes of OLEDs, schematically illustrated in Fig. 5. Once holes and electrons are bound together, excitons could be generated and thus undergo radiative and non-radiative process. Photons are detectable once excitons created in the EML are strongly radiative. This is a typical mechanism of an working OLED. Ideally, the emissive colors depend closely on the bandgaps of the emitters which are equivalent to the difference between the lowest unoccupied molecular orbitals (LUMOs) and the highest occupied molecular orbitals (HOMOs).



Fig. 4 Photos of OLED lighting products by courtesy of First Light Technology. Reproduced from Yiguang, 2021. 'About us' [Online]. Available at: <http://www.first-oled.com/gongsijiejian2/> (September 2021).

An ideal OLED requires the barrier-free injection of charge carriers. However, it is challenging to match the energy level alignment of each layer. Therefore, the device with the stepwise barriers are constructed to ensure low ohmic loss and high radiative recombination rate. The current flow is a nonlinear function of the driving voltage, which could be approximately described by using a diode equation (see below).

$$J(V) = J_0 \left[\exp\left(\frac{eV}{nk_B T}\right) - 1 \right] \quad (1)$$

where J_0 is the saturation current, e the elementary charge (1.6×10^{-19} C), n the ideality factor of the diode, k_B the Boltzmann's constant (1.38×10^{-23} J/K), and T the temperature in Kelvins.

According to Ohm's law, the drift current in the diode-like semiconducting devices could be described as Eq. (2).

$$J(E) = \sigma(E)E \quad (2)$$

where E is the electrical field and $\sigma(E)$ is the conductivity which follows Eq. (3).

$$\sigma(E) = ne\mu(E) \quad (3)$$

where n is the concentration of charge carriers and $\mu(E)$ the mobility of charge carriers (either holes or electrons). In organic semiconductors, the mobilities, typically ranging from 10^{-6} to 10^{-1} $\text{cm}^2/(\text{V} \cdot \text{s})$, depend on the electrical field and are significantly lower than those of the inorganic counterparts, which account for the insufficient conductivities. The conductivities of organic semiconductors mainly locate in the gap between Si and PEDOT:PSS show in Fig. 6.

In terms of thin device (~ 100 nm), the current of the single carrier device, i.e., hole- or electron-only, tends to be space charge limited, i.e., SCLC, if the injection contact is ohmic (Blom *et al.*, 1996). Therefore, the current-voltage characteristics follow Eq. (4).

$$J(E) = \frac{9}{8} \frac{\varepsilon \varepsilon_0 V^2}{d^3} \mu(E) \quad (4)$$

where ε is the dielectric constant, ε_0 the permittivity in free space (8.85×10^{-12} F/m), and d the thickness of organic film. Rigorously, the mobility exhibited the electrical field dependency (Murgatroyd, 1970).

$$\mu(E) = \mu_0 \exp(0.89\beta\sqrt{E}) \quad (5)$$

where β is the field dependent constant. To address the issue of Ohmic contact in organic semiconducting devices, Prof. Leo developed the electrical doping strategy and founded the spin-off company Novaled which was acquired by Samsung SDI in 2013 (Novaled, 2021). This technology makes OLEDs more stable and less power consumption and more flexible to integrate with the active matrix driving circuits.

Excitons

As mentioned previously, the bound hole-electron pairs form excitons. According to the Pauli Exclusion principle, only two electrons with the opposite spin states, i.e., spin-up ($+\frac{1}{2}$) and spin-down ($-\frac{1}{2}$) electrons, could occupy the same orbital. If zero net angular momentum is achieved in a quantum mechanics state with two spin particles ($\pm\frac{1}{2}$), it is a singlet state. In a triplet state,

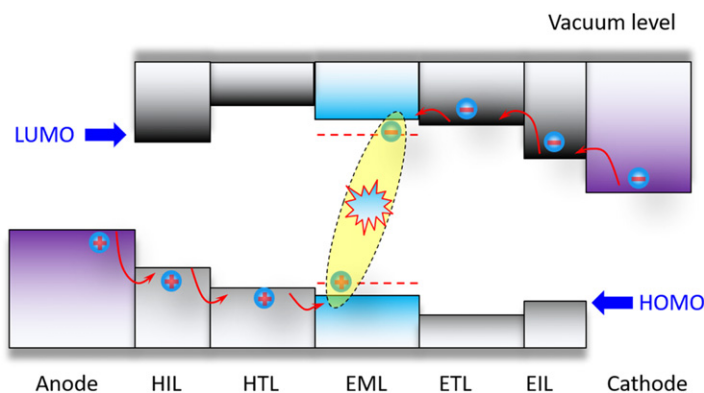


Fig. 5 Schematic diagram of energy level alignment in an OLED.

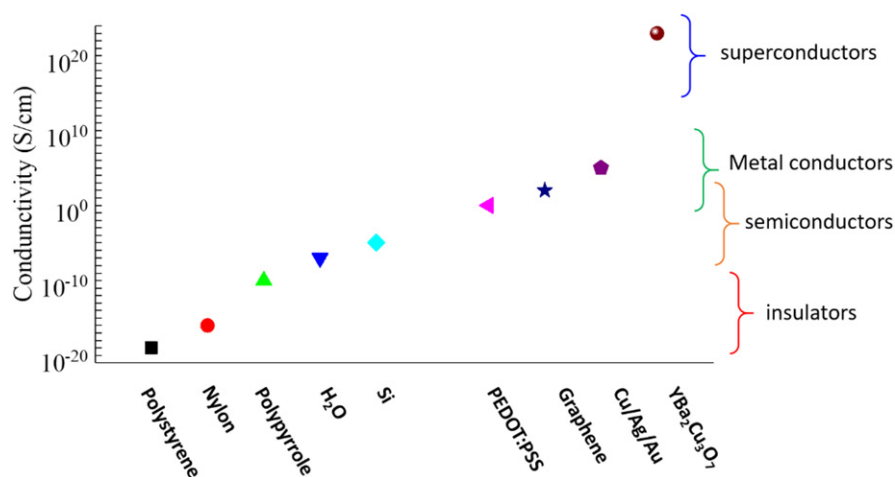


Fig. 6 Comparison of conductivity.

the total spin quantum number equals 1, which corresponds to three allowed numbers of the spin components (0, -1 and +1). According to the spin statistics, the singlet to triplet ratio is 1:3 under the electrical excitation, following the Boltzmann distribution. Fig. 7 illustrates some of the radiative and non-radiative transitions in a typical organic emitter. S_n ($n = 0, 1, 2, \dots$) stands for the singlet states and T_m ($m = 1, 2, \dots$) for the triplet states. The radiative processes directly from the singlet and triplet states refer to fluorescence and phosphorescence.

The photoluminescent quantum yield of an emitter closely correlates with the radiative and non-radiative processes of the excitons. By measuring the photoluminescent quantum yield (Φ) and the transient lifetime (τ), one could roughly estimate the rate constants with Eqs. (6) and (7). In a real condition, there are the complicated and entangled excitonic processes. Thus the multiple exponential decay curves could be detected (see Fig. 8). The simplify to evaluation of the rate constants, the averaged excitonic lifetime could be weighted based on the amplitudes of the curve fitting.

$$k_r = \frac{\Phi}{\tau} \quad (6)$$

$$k_{nr} = \frac{1 - \Phi}{\tau} \quad (7)$$

Luminescent Mechanisms and The Emitters

A booming market of OLED smartphones has been witnessed in the last few years. To meet the requirements of the consumers, chasing high degree of cost-effectiveness is an unending topic. Evidenced in Fig. 9, molecular design is one of the most important and basic approaches to address this issue. Currently, the state-of-the-art smartphones most likely are implemented with blue fluorescent emitters and red/green phosphorescent emitters to realize full-color displays. Those emitters are applicable to OLED lighting in terms of achieving high color rendering indexes. Singlet and triplet excitons are frequently discussed in the luminescent

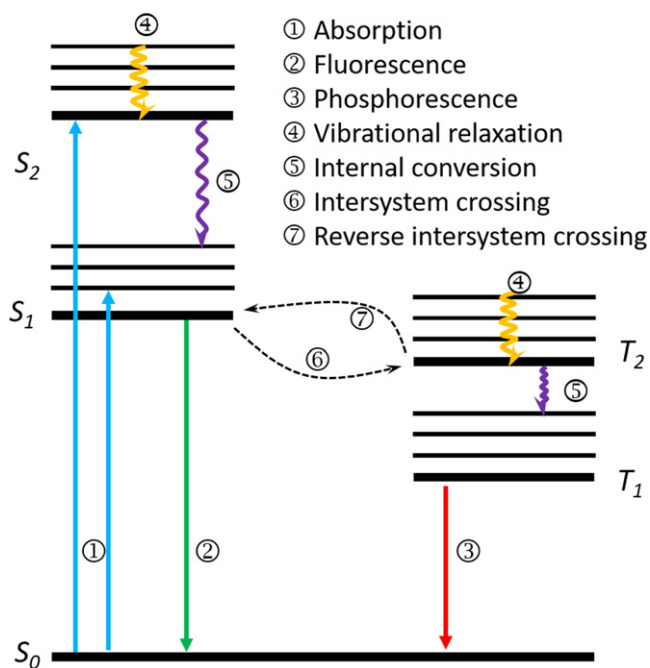


Fig. 7 Simplified Jablonski diagram illustrating the possible transitions in an organic emitter. Reproduced from Pope, M., Swenberg, C.E., 1999. *Electronic processes in organic crystals and polymers*, second ed. Oxford University Press.

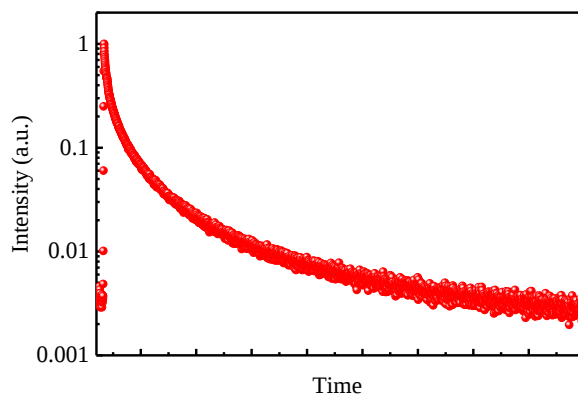


Fig. 8 Example of an organic emitter with the multiple exponential transient decays.

mechanisms of OLEDs (Sun *et al.*, 2006; Goushi *et al.*, 2012). Nevertheless, doublets, which originate from two allowed values of the spin component in a quantum state with the spin angular momentum of either $+\frac{1}{2}$ or $-\frac{1}{2}$, are found to be efficiently generated and converted into photons in the EL processes (Ai *et al.*, 2018). Overall, singlet, doublet, and triplet could be described by a universal multiplicity equation, i.e., $2s + 1 = 1, 2$, and 3 , where s is the net/total spin angular momentum.

Fluorescent Emitters

Due to the opposite spin status of the electrons in the excited states of fluorescent emitters, the triplet excitons are non-radiative. As illustrated in Fig. 10(a), the maximum internal quantum efficiency (IQE) of a fluorescent emitter is only 25%, which limits the external quantum efficiency (EQE) of the device at about 5%. Above all, it is relatively easy to synthesize the fluorescent emitters due to the simple molecular structure. In addition, the fluorescent molecules are commonly stable. Originated from the local excited emission and thus the reduced structural/excited state relaxation, the full-width-at-half-maximums (FWHMs) of the fluorescent spectra are frequently found to be 30–50 nm in the state-of-the-art emitters, which are favorable for high color-purity and wide color-gamut displays (Chao *et al.*, 2005; Luo *et al.*, 2007; Liu *et al.*, 2007; Kim *et al.*, 2001; Shih *et al.*, 2007). Therefore, blue fluorescent emitters are much more cost-effective in the state-of-the-art OLED display and lighting products (Wen *et al.*, 2005; Zhu and Yang, 2013).

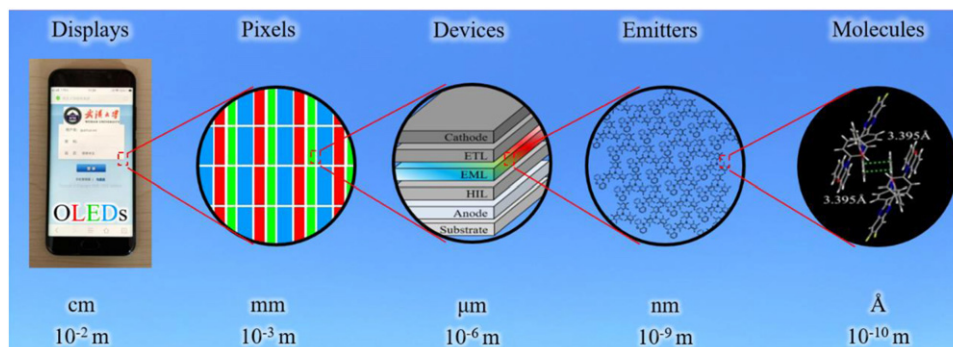


Fig. 9 Illustration of OLED units in a smartphone.

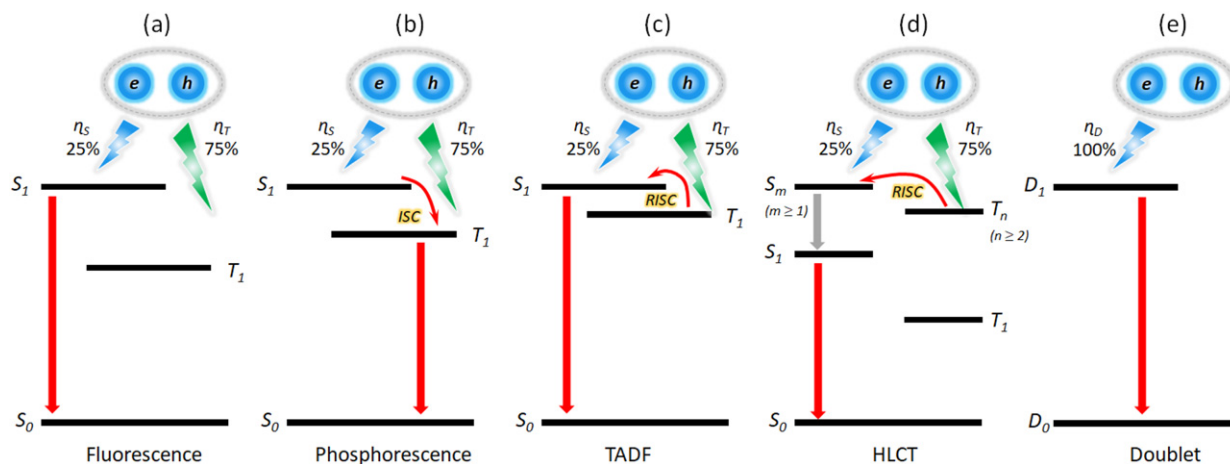


Fig. 10 Simplified schematic diagram of different EL mechanisms of organic emitters.

Most of fluorescent emitters encounter with concentration-caused quenching (ACQ) effect. Thus host-guest doping strategy is usually introduced to disperse the emitter and align the energy levels for charge carrier injection/transport. However, non-doped or self-host fluorescent emitters are achievable by modifying the molecular structures and packing modes to reduce intermolecular interaction (Kim *et al.*, 2005; Wu *et al.*, 2009; Kim *et al.*, 2008). As an emerging luminescent compounds, the fluorescent emitters with the aggregation-induced emission (AIE) features are good candidates for fluorescent OLEDs without doping (Shi *et al.*, 2015; Huang *et al.*, 2013; Li *et al.*, 2019).

As a specific case, triplet-triplet annihilation (TTA) in fluorescent emitters provides a unique strategy to harvest the non-radiative triplet excitons, which could contribute to the IQE exceeding spin statistical limit of 25% (Kondakov, 2015; Luo and Aziz, 2010; Kondakov *et al.*, 2009). In the point of molecular design, TTA emitters for fluorescent OLEDs require the low T_1 level approximately at half energy of T_2 . Experimentally, TTA is detectable in presence of the delayed fluorescence and the slope of the photoluminescent intensity vs. the excitation energy should be 2 ascribed to the bimolecular recombination (Serevičius *et al.*, 2017).

Phosphorescent Emitters

Since the two independent pioneering researches of heavy-metal complexes for OLED applications in 1998, (Baldo *et al.*, 1998; Ma *et al.*, 1998) phosphorescent emitters attract both intensive interest from academic and industry. The state-of-the-art OLED smartphones basically utilize the red/green phosphorescent dopants to reduce the power consumption since 100% IQE is theoretically and experimentally obtainable. As displayed in Fig. 10(b), the energy of the singlet excitons could be harvested by the triplet excitons and all of the triplets could be recombine radiatively due to the spin-orbital coupling induced by the heavy atoms, e.g., iridium and osmium.

One of the challenging topics in phosphorescent emitters is the stable blue emission. Due to the low bond dissociation energy of blue phosphorescent emitters, the operational lifetimes of the devices lag far behind the blue fluorescent counterparts. Although some breakthroughs of blue phosphorescent emitters and devices have been achieved for commercial applications by the leading companies, e.g., UDC, they are proprietary and highly costly (Universal Display Corporation, 2021). The cutting research of phosphorescent emitters focuses on low-cost, highly stable and efficient compounds with the satisfied charge transport and short

excitonic lifetimes. They are not only limited to the iridium family but also extendable to other candidates, such as gold and platinum complexes (Tang *et al.*, 2021).

TADF Emitters

At the presence of a small ΔE_{ST} , the triplet excitons can be up-converted to the singlet states via RISC process, which leads to the transition to the ground state and simultaneously radiative decay (see Fig. 10(c)). The delayed fluorescence ascribed to the above-mentioned mechanism is dominated by thermal activation, which is one of the characteristics of TADF and contributes to the potential 100% exciton utilization. In the last 10 years, many molecular design strategies have been proposed to make a good TADF emitter (Wong and Zysman-Colman, 2017; Liu *et al.*, 2018; Yang *et al.*, 2017; Zheng *et al.*, 2020). In general, through-bond and through-space charge transfer account for the generation of TADF behaviors in purely organic compounds with the donor and acceptor moieties (Xue and Xie, 2021). Nevertheless, some metal (e.g., Cu, Ag, and Pd) complexes have been reported with the TADF phenomenon, without the strong spin-orbit coupling (SOC) required with the heavy metals featuring phosphorescent emission (Yersin *et al.*, 2017; Zhu *et al.*, 2015). Apart from the intramolecular strategy, TADF could be triggered by the intermolecular interactions, e.g., exciplex induced from a donor and an acceptor molecules (Graves *et al.*, 2013; Sarma and Wong, 2018).

The freedom in molecular design makes TADF compounds ideal for cost-effective OLEDs. However, the broadband emission attributed to the charge transfer nature, typically featuring a FWHM of 60–100 nm, is less competitive for high color-purity displays. Recently, a new strategy called multiple resonance was demonstrated as an effective approach to restrict the excited state relaxation and thus narrow the FWHMs of TADF emitters down to ca. 20 nm, which are very competitive with the quantum-dot emitters (Hatakeyama *et al.*, 2016; Yuan *et al.*, 2019). However, such TADF emitters have very rigid frameworks which result in concentration quenching, poor solubility and difficulty in color tuning. To address these issues, extension of aromatic rings, introduction of *tert*-butyls, polymerization, and conjugation manipulation are found to be effective (Xu *et al.*, 2021a; Chen *et al.*, 2021; Yang *et al.*, 2020).

HLCT Emitters

Triplet up-conversion from higher triplet level (T_n , $n \geq 2$) via RISC channel to the singlet states (S_m , $m \geq 1$), which is also regarded as “hot exciton” process, is typically less common and efficient in organic emitters. In 2012, Ma’s group manipulated the excited state with hybridized local and charge-transfer (HLCT) properties (see Fig. 10(d)) and designed a new fluorescent compound with deep-blue color and a high exciton utilization ratio of 28% in the multi-layered OLED, which surpassed the upper limit (25%) of the conventional fluorescent devices (Li *et al.*, 2012). In the presence of the “hot exciton” mechanism, an emitter with the HLCT properties is capable of all of the electrically generated excitons and thus reaches an unity exciton utilization. However, it is worth noting that many molecules functioned with the HLCT properties didn’t exhibited the “hot exciton” mechanism and thus poor EL performances (Xu *et al.*, 2021b). One of the key issues to construct efficient HLCT emitters for efficient OLEDs is to awaken the “hot excitons” by minimizing the energy gap between S_m ($m \geq 1$) and T_n ($n \geq 2$) mentioned above. Different to the common TADF emitters, an efficient HLCT emitter with hot excitons could simultaneously possess the merits of high photoluminescent quantum yield, short exciton lifetime, and small FWHM, which are ideal for high-end OLED displays. Nevertheless, it is currently challenging to design the efficient HLCT emitters respectively with red/green/blue colors and high stability under the electrical driving.

Doublet Emitters

Most of the emitters for OLED applications have a common closed-shell structure. Based on the spin statistics, the ratios of singlet and triplet excitons are 25% and 75%, respectively generated under the electrical field. In contrast, the open-shell compounds, e.g., radicals with only one electron in the outermost molecular orbital are reported with the totally different spin configuration, i.e., doublet excitons. As shown in Fig. 10(e), the transition from D_1 to D_0 contributes to doublet emission, which allows 100% exciton utilization. In 2015, Li’s group reported the first doublet-based OLEDs with a radical emitter doped in the common organic host and achieved an EQE of 2.4% and an EL peak of 692 nm (Peng *et al.*, 2015). By modifying the peripheral structure of the radical core, the highly efficient infrared radical OLED was demonstrated with a considerably high EQE of 27%, which provided the solid proof of unity doublet utilization under EL process (Ai *et al.*, 2018). Since the doublet-based OLEDs are limited to the narrow bandgap neutral π monoradicals and the derivatives, currently, the researchers are struggling to design and find the blue and green candidates with the open-shell and doublet nature.

Device Architecture, Optical Modes, and Fabrication

Device Architectures

Due to the amorphous nature, organic semiconductor films could be easily grown layer-by-layer on many kinds of substrates, e.g., no matter rigid, flexible, opaque, or transparent. Depending on the direction of light beams coming out from the devices, there would be bottom-emitting OLEDs (BEOLED) with the opaque top electrode, top-emitting OLEDs (TEOLEDs) with the opaque bottom

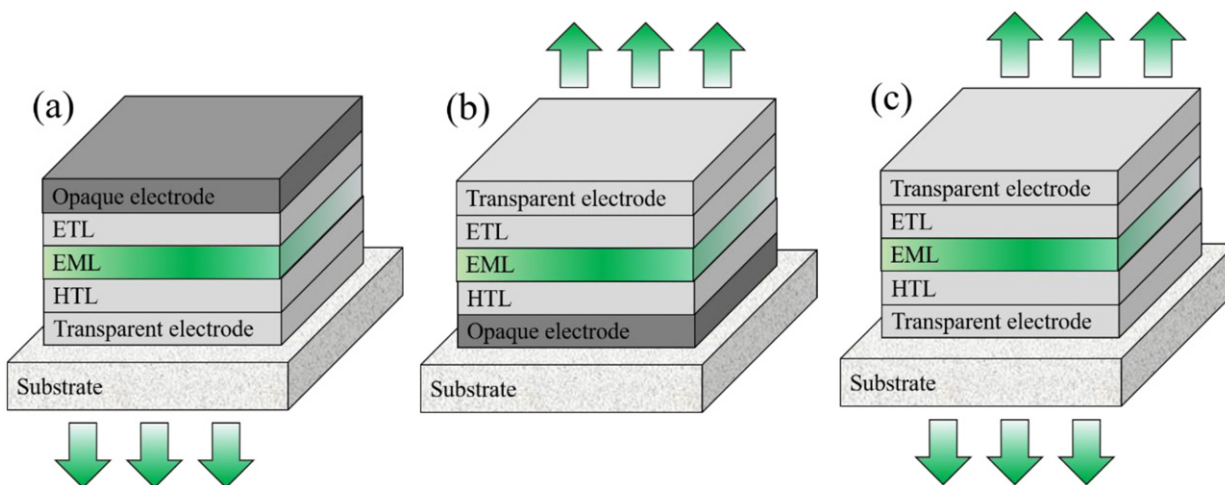


Fig. 11 Schematic diagram of the device structures: (a) bottom-emitting, top-emitting, and see-through/semitransparent OLEDs.

electrode, and (semi)transparent OLEDs, schematically shown in **Fig. 11** (Xie *et al.*, 2010; Görm *et al.*, 2006). TEOLEDs are more favorable for the high resolution smartphones, owing to the high aperture ratio (Blochwitz-Nimoth *et al.*, 2004).

As illustrated in **Fig. 12**, tandem device could be constructed by stacking several units with the charge generation layer (CGL) which plays an important role in improving hole/electron generation and thus the EL efficiencies. Ideally, the EQE of the tandem device is proportional to the numbers of the sub-device. Although the driving voltage will be increase in the tandem structure, the stability will be significantly improved ascribed to the lower current density required at a desired luminance, compared with the non-tandem device. Unlike stacking the identical unit shown in **Fig. 12(a)**, white color, such as color temperature and color rendering index, could be feasibly tuned in a wide range by changing the individual R/G/B compositions and sequence of the sub-devices shown in **Fig. 12(b)**.

Flexible and stretchable OLEDs are available when the electrodes and the organic films are deposited on the flexible and stretchable substrates, respectively. One of the challenging issues is to develop the highly flexible electrodes, e.g., thin metal layer or metal mesh/conductive polymer composites. For practical applications, the flexible and stretchable encapsulation schemes become more troublesome since any cracks and defects provide the very efficient oxygen/water vapour transmission channels.

Optical Modes of OLEDs

OLEDs are surface light sources in the presence of the planar thin-film structure shown above. Due to the different refractive indexes of the organic layers, the electrodes, and the substrates, most of the light beams generated in the EML are trapped inside the device itself. The EQE is described as below (Archer *et al.*, 2021).

$$\eta_{EQE} = \gamma \times \Phi \times \eta_r \times \eta_{oc} \quad (8)$$

where η_{EQE} is the external quantum efficiency, γ charge balance factor, Φ photoluminescent quantum yield, η_r radiative recombination ratio, and η_{oc} light outcoupling efficiency.

Taking BEOLED as an example, there are substrate mode, waveguided mode, absorption loss, evanescent coupling loss, and air mode (out-coupled component). Since the light beams come out in the opposite direction of the substrate, there is no substrate mode but elevated evanescent loss when the semi-transparent metal contact is employed (see **Fig. 13**). For isotropic emissive dipoles in common BEOLEDs with the ITO anode, the out-coupling efficiency is estimated as 20%–30%, assuming the refractive indexes of ITO, the glass substrate, and the organic layers (ca. 100 nm) are 2.0, 1.5, and 1.7, respectively. By manipulating the horizontal orientation of the emissive dipoles and refractive index of the substrate, an EQE over 80% has been demonstrated in the planar OLED (Wang *et al.*, 2021).

Fabrication Approaches

Fabrication approaches of OLEDs are basically categorized into dry and wet processes (Koden, 2016; Ho *et al.*, 2015). The dry process closely relies on vacuum deposition. For small molecules, the molecular mean-free-path dramatically increases when the vacuum pressure drops. Organic compounds typically with molecular weights less than 1000 g/mol, tend to be sublimable if they are stable enough under heating at ca. 100 ~ 300°C. Empirically, the mean-free-path is up to 1 m at a pressure $10^{-4} \sim 10^{-5}$ Pa. This allows the design and fabrication of very complicated and unlimited organic layers. Therefore, most of the current foundries of OLED panels are adopting the thermal evaporation techniques although they are very expensive.

To make OLEDs more affordable for displays and lighting products in the market, the wet processes, e.g., spin-coating, blade-coating, spray-coating, screen printing, roll-to-roll, and inkjet printing, have been developed for OLED fabrication. The wet processes have more freedom in selecting the organic materials, including small molecules, dendrimer, and polymers which

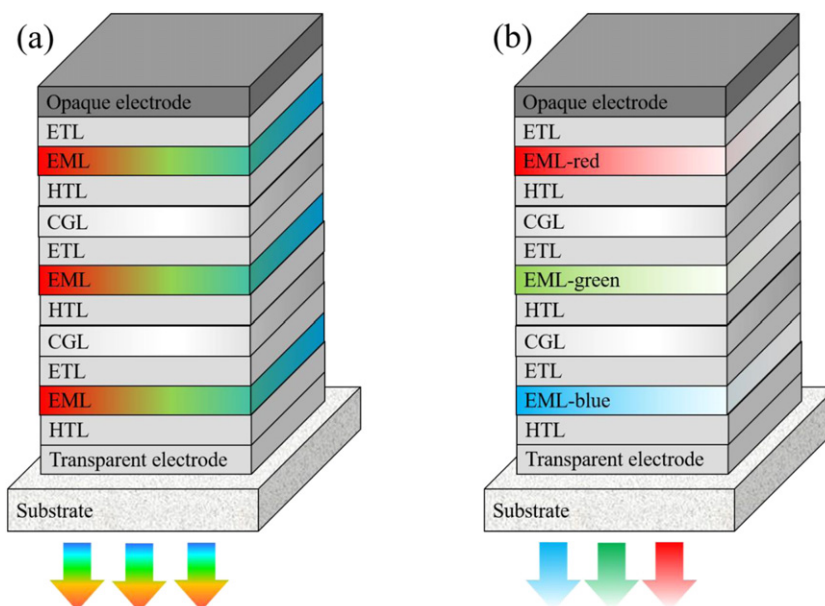


Fig. 12 Example tandem device structures: (a) repeating sub-device with the identical emissive color and (b) different sub-device with several colors.

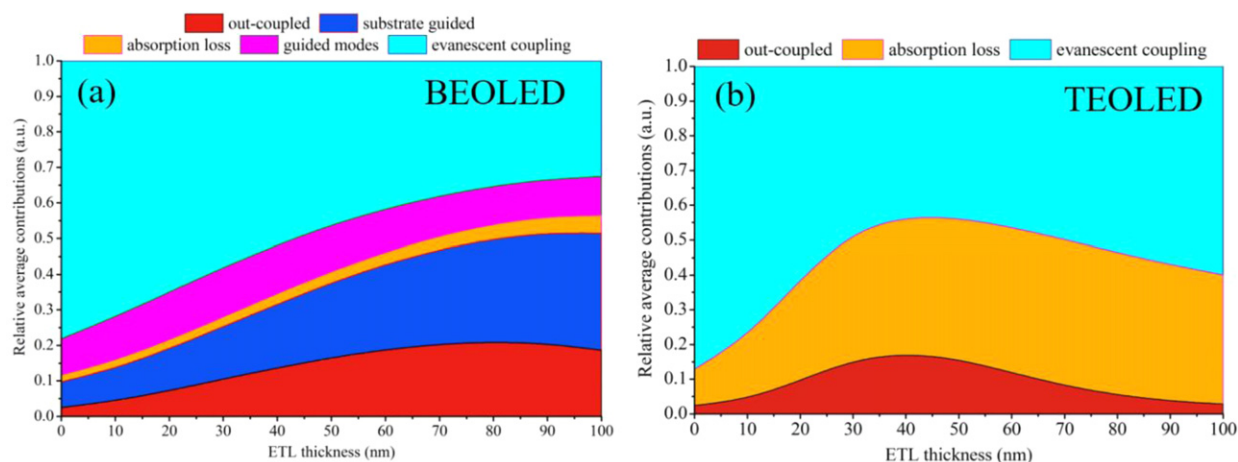


Fig. 13 Example optical mode distribution of (a) bottom-emitting OLED (BEOLED) and (b) top-emitting OLED (TEOLED) as a function of the thickness of the ETL, assuming the dipoles are located at the vicinity of the interface between the EML (20 nm) and the ETL (40 nm).

should meet the requirements of the satisfied solubility in the processing solvents and thus good film quality after processing. The wet processes highly depend on the orthogonal solvents once the multi-layer structure is needed to maximize the EL performances. The cross-linking strategy provides a good approach to deposit the multi-layer solution-processed OLEDs. However, it is a challenging issue to develop the cross-linked organic compounds simultaneously matched well the morphological, optical and electrical requirements of OLEDs. Alternative to the orthogonal solvent scheme, the composite processes would be a good option. For instance, transfer printing is found possible to grow and pattern polymer on small molecular layer with the distinct interface and thus demonstrate efficient and bright OLEDs (Tang *et al.*, 2019).

Characterization and Device Performances

There are two lab-based schemes for determining the EL properties of OLEDs, frequently found in the literatures. A spectro-radiometer combined with the source measure unit provides a solid setup to evaluate the EL performances of OLEDs. However, the spectroradiometer is relatively expensive and the measurement rate is lower and dependent on the luminance level. Therefore, the alternative scheme of the calibrated Si photodiode combined with the source measure unit become more popular although the

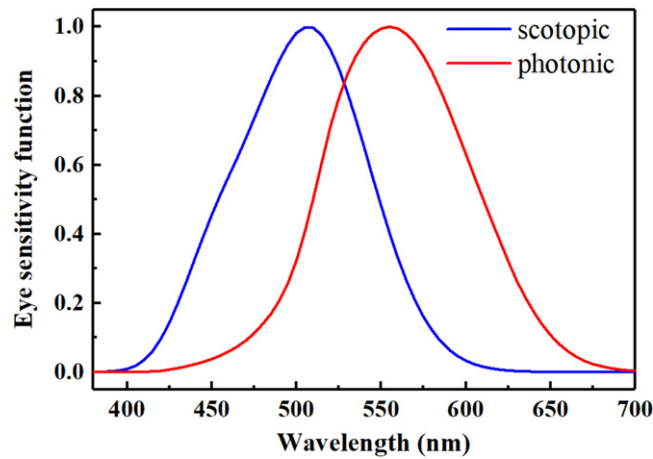


Fig. 14 Comparison of the scotopic and photonic curves. Data extracted from Reference Anon3, 2021. Hyperphysics 'Luminous efficacy' [Online]. Available at: <http://hyperphysics.phy-astr.gsu.edu/hbase/vision/bright.html> (September 2021).

setup requires very strictly calibration (Forrest *et al.*, 2003). Nevertheless, direct measurement of the EQE could be implemented with an integrated sphere. Empirically, the response and accuracy at low luminance levels are not satisfied when using an integrated sphere.

In general, the EQE is defined as the ratio of the total number of the emitted photons (N_p) divided by the total number of the electrons injected into the device (N_e), which are respectively described as below (Archer *et al.*, 2021; Okamoto *et al.*, 2001).

$$N_e = \frac{I_e}{e} \quad (9)$$

I_e is the radiant intensity and e is the elementary charge.

$$N_p = \frac{1}{hc} \iint \lambda I(\lambda, \Omega) d\lambda d\Omega \quad (10)$$

Here, θ and φ are the polar coordinates in a spherical geometry, ranging from 0 to $\frac{\pi}{2}$ and from 0 to 2π , respectively. $I(\lambda, \Omega)$ is the spectral radiant intensity as a function of the solid angle. For a common planar OLED, the angular emissive profile normally follows a Lambertian pattern, which derives Eq. 11.

$$I(\lambda, \theta) = I_0(\lambda) \cos(\theta) \quad (11)$$

In order to calculate the EQE, all the photons emitted over the entire solid angle Ω should be collected. Then the solid angle reads as below.

$$\Omega = \iint \sin(\theta) d\theta d\varphi \quad (12)$$

Therefore, the total number of photons could be rewritten as Eq. 13.

$$N_p = \frac{1}{hc} \iiint \lambda I_0(\lambda) \cos(\theta) \sin(\theta) d\lambda d\theta d\varphi \quad (13)$$

Based on Eq. 14, the solid angle Ω equals to π .

$$\int_0^{\frac{\pi}{2}} \cos(\theta) \sin(\theta) d\theta \int_0^{2\pi} d\varphi = \pi \quad (14)$$

Then the general EQE calculation is simplified as below.

$$\eta_{EQE} = \frac{N_p}{N_e} = \frac{\pi e}{h c} \int_{380}^{780} \lambda I_0(\lambda) d\lambda \quad (15)$$

where h is Planck's constant and c is the velocity of light.

Considering the response of human eye, the luminance is given as Eq. 16.

$$L = \int_{380}^{780} L(\lambda) d\lambda \quad (16)$$

For an OLED emits in the visible range, the photons reads as below.

$$N_p(\lambda) = \frac{\pi \lambda L(\lambda)}{683 h c V(\lambda)} \quad (17)$$

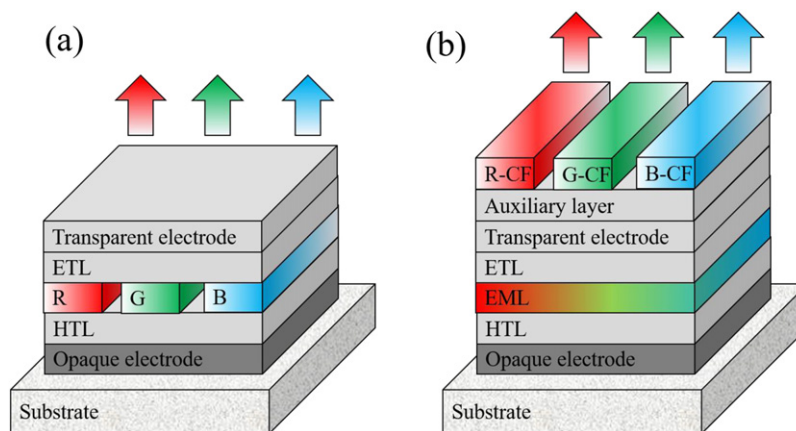


Fig. 15 Comparison of full-color OLED display schemes: (a) direct red/green/blue sub-pixels and (b) white emitting layer + color filters.

$V(\lambda)$ is the photonic efficiency function of human eye. It is worth mentioning that the spectral luminous efficacy for human vision varies at different brightness background. As shown in Fig. 14, the maximum scotopic efficacy is 1700 lm/W at 507 nm while the maximum photopic efficacy is 683 lm/W at 555 nm (HyperPhysics, 2021).

Moreover, the current efficiency (CE) and the power efficiency (PE) are derived as Eqs. 18 and 19.

$$CE = \frac{LA}{J} \quad (18)$$

J is current and A is the emissive area

$$PE = \pi \frac{CE}{V} = \pi \frac{LA}{JV} \quad (19)$$

V is the driving voltage. In order to achieve high PE, the driving voltage should be reduced.

OLED Applications

As one of the emerging display technologies, OLED could be driven under either passive or active matrix mode. There is no storage capacitor in passive matrix OLEDs (PMOLEDs) (Haskal *et al.*, 2002). The pixel is turned off immediately once the voltage pulse is off. Despite of the simple layout of the driving circuits, the row and line based interdigitated anode and cathode easily result in the electrical crosstalk if high density pixel array is employed. Therefore, PMOLEDs are only used in low-information-content displays, such as MP3 player, digital watch, and some other small-size screens. In contrast, active matrix OLEDs (AMOLEDs) are constructed with much more complicated driving circuits including at least one capacitor and the thin-film transistors as the driving backplane (Dawson and Kane, 2012). This design allows high refresh rates, high resolution, and wide range of panel sizes covering the smartphones, laptop, and also TVs. Beyond smartphones, flexible and automobile displays based on AMOLEDs are leading a new wave of display innovation. In terms of full-color displays, no matter PMOLEDs or AMOLEDs, they share similar color mixing schemes. As shown in Fig. 15(a), the direct Red/Green/Blue patterns driven by the individual pixel could cut off the power consumption but require several masking process to define each color. There is no masking requirement for the scheme of white light + color filters which are patterned and fabricated outside the OLED unit (see Fig. 15(b)). Since each color filter absorbs ca. 70% of the white light energy, the power consumption of such device are higher at the same driving mode. Above all, new algorithms could be employed to save the power consumption which depends on the display contents.

OLED Lighting is supposed to be one of the most healthy lighting technologies since very limited blue light in the range of 410–430 nm will be used (Hack *et al.*, 2017). The color temperature and color rendering index could be easily tuned to mimic sunlight during the daytime. Moreover, the reduced blue light hazard may have positive physiological and psychological effects. OLEDs as the signage applications are also promising. For example, automobile tail light based on OLEDs is very effective in reducing the dazzle effect.

Efficient red/infrared OLEDs might found useful applications in photodynamic therapy. Unlike inorganic LEDs, OLEDs have wide FWHMs and could be feasibly deformed to human skin. For photodynamic therapy, deep-red OLEDs with low-irradiance were reported effective in curing the skin cancer with less pain during and after the treatment for the patients (Attili *et al.*, 2009).

Visible light communication is supposed to be one of the game changers in the ear of internet-of-things. OLEDs are bio-friendly and eye-safe, which is very unique for visible light communication. However, due to the intrinsically large capacitance as a surface light source, normal OLEDs exhibits a transient EL lifetime in the scale of μ s, which limits the transmission data rate. For example, near infrared OLEDs mainly covering the range of 650 ~ 800 nm could achieve a data rate of 2.2 Mb/s (Minotto *et al.*, 2020). The deliberated device engineering and the EML with the shorter exciton lifetime are required to improve to energy and spectral efficiencies and data rates.

Outlooks

The development of OLED technology has experienced a great success during the last 3 decades. Exciton generation and utilization under PL and EL processed are discussed and compared. Based on molecular innovation and discovery of new luminescent mechanisms, the internal quantum efficiency of 100% are achievable. To make OLED more efficient, the out-coupling strategies should be carefully considered based on dipole orientation and optical mode analysis. To make OLEDs more affordable, it is very urgent to address the issues of cost and stability, especially for blue materials and devices. OLEDs are versatile and the flexibility and stretchability make OLEDs more competent in the near future.

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<https://en.oledspace.com/>—Transparent OLED - LG Display - OLED SPACE

Small Molecule versus Polymer Semiconductors

Maryam Shahi and Alexandra F Paterson, University of Kentucky Center for Applied Energy Research, Lexington, KY, United States

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Abstract

Over the years, two prominent materials categories have emerged for organic semiconductors: small-molecules and polymers. On one hand, small-molecules have high crystallization propensity and subsequent high mobilities, but their crystalline structures simultaneously make it difficult to control their microstructures during solution-processing. On the other hand, polymers have excellent film-forming qualities because of their long chains, which simultaneously introduce intrinsic disorder, thereby lowering the mobility. The article herein discusses this intrinsic small-molecule versus polymer trade-off in the context of solution-processing. Namely, its background/history and ways to overcome it, to achieve the plastic electronic goal of solution-processed semiconductors with high electronic performance.

Nomenclature

Symbol/Name Description.

$B(C_6F_5)_3$ Lewis acid tris(pentafluorophenyl)borane.

BTBT [1]benzothieno[3,2-*b*][1]- benzothiophene.

C_8 -BTBT 2,7-Dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene.

C_{16} IDT-BT indacenodithiophene-benzothiadiazole.

C-AFM Conductive atomic force microscopy.

diF-TES ADT 2,8-Difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene.

E Electric field (V/cm).

E_σ Energy level of σ orbital (eV).

E_{σ^*} Energy level of σ^* orbital (eV).

HOMO Highest occupied molecular orbital.

IDT indacenodithiophene (4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene).

LUMO Lowest un-occupied molecular orbital.

OECT organic electrochemical transistors.

OLEDs light emitting diodes.

OPV organic photovoltaics.

OSC Organic semiconductor.

OTFT organic thin-film transistors.

P3HT poly(3-hexylthiophene).

PF-TAA poly(dioctylfluorene-co-bis- N,N' (2,4-dimethylphenyl) diphenylaminedimethyl).

PMMA 3,11-didecyldinaphtho[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (C_{10} -DNBDT-NW):poly(methyl methacrylate).

PTAA poly(triarylamine).

P α MS poly(α -methylstyrene).

Rubrene 5,6,11,12-tetraphenyltetracene.

TES-ADT 5/11-triethylsilylethynyl anthradithiophene.

TIPS-pentacene 6,13-Bis(triisopropylsilylethynyl)pentacene.

V Drift velocity (cm/s).

$Zn(C_6F_5)_2$ Lewis acid, bis(pentafluorophenyl)zinc.

Ψ_π In phase bonding orbital formed due to overlap of two sp^2 orbitals.

Ψ_{π^*} Out of phase bonding orbital formed due to overlap of two sp^2 orbitals.

Ψ_σ Bonding orbital formed due to overlap of two $2p_z$ orbitals.

Ψ_{σ^*} Anti-bonding orbital formed due to overlap of two $2p_z$ orbitals.

sp^2 Molecular orbital formed after 2s orbitals combines with two of the 2p orbitals.

μ Mobility (cm^2/Vs).

Introduction

Semiconductors are functional materials that have demonstrated extreme disruptiveness over the last decades. The digital revolution and widespread implementation of modern electronic devices is underpinned by the ability to control electronic conductivity, within this class of functional materials. The resultant impact is the greatest in modern history: creating an electronic human landscape has altered communication and the standard of living. Behind this great evolutionary phase is silicon, the

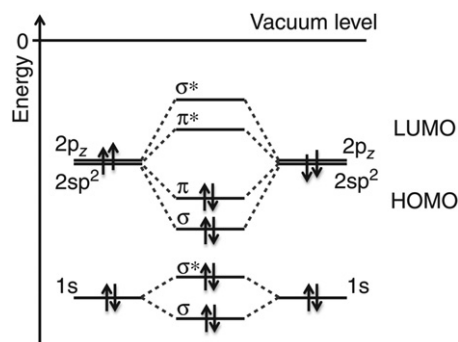


Fig. 1 Energy level diagram showing what happens when two carbon atoms interact, namely the formation of σ - and π -bonds. The highest occupied molecular orbital (HOMO) is the bonding π -orbital. The next level is the antibonding π^* -orbital; it is empty and referred to as the lowest unoccupied molecular orbital (LUMO). Diagram is reproduced with permission from reference Anna Köhler, H.B., 2015. The electronic structure of organic semiconductors. *Electronic Processes in Organic Semiconductors* 1–86.

fundamental semiconductor. However, silicon is expensive – with batch processing requiring high temperatures – and only offers limited, fixed mechanical properties. Emergent semiconductors that exhibit alternative or beneficial properties, when compared to silicon, have therefore attracted broad interest in both academic- and industry-led research environments.

One emergent class of semiconductor offering potential for novel electronic application/technology development, are plastic or organic semiconductors (OSCs). The plastic electronics field has attracted significant interest in recent years and rapidly continues to do so. The origin of this interest lies with OSC low cost, processing versatility and unique mechanical properties: imagining electronics processed at the same economic cost as existing, commercial plastics, and with weak molecular bonding (van der Waals), requiring less energy to manipulation, that makes them ideal for flexible, foldable, and stretchable electronics – much unlike incumbent silicon. Furthermore, the many options for chemical synthesis leads to a broad pallet of OSC structures as well as the idea of “make to order” electronics with tailored electronic properties.

The key quality often attracting interest above of all these points, is that fact that OSCs are solution processible, because they are easily dissolved in solvents. This enables extreme processing versatility and offers a great advantage over silicon. For example, large-area printing techniques, roll-to-roll processing, and in more recent years other novel approaches such as drawing electronic fibers from solution to create electronic textiles. However, such processing versatility also presents a double-edged sword: there is a direct relationship between microstructure/order and electronic properties, and solution-processing leads to a wide variety of OSC morphologies, and therefore a wide variety of (or, non-uniformity in) electronic properties. This intrinsic variation is difficult to control and can lead to unreliable microstructures – principally unlike silicon, which goes through multiple, rigorous steps and well-characterized Czochralski growth to process single-crystal boles boules. The fundamental relationship between physical structure, electronic properties and processing is therefore of enormous importance. Solution-processing techniques must be carefully optimized and understood, and the task of generalizing such processing techniques for the broad pallet of synthetically available OSCs is challenging. This relationship impacts the properties/success of the traditional “big three” – organic light emitting diodes (OLEDs), organic thin-film transistors (OTFTs), and organic photovoltaics (OPVs) – as well as up and coming organic technologies such as organic electrochemical transistors (OECTs) and electronic textiles, for sensing, bioelectronic, neuromorphic and energy storage applications.

Broadly speaking, if an OSC layer exhibits a high degree of crystallinity, it will also exhibit enhanced electronic transport. OSCs with a less structured (more disordered) or amorphous structure have reduced electronic properties. Over the years two key OSC categories have emerged that define this rule: (1) small-molecules and (2) polymers. There is enhanced charge transport in small-molecules versus polymers, because of their crystalline structure, which has been shown systematically throughout the literature and is primarily shown as higher measured mobility in OTFTs. However, despite small-molecules promising higher mobilities, they are more difficult to process controllably from solution, which in turn reduces such measured mobility values. Polymers, on the other hand, are easier to process from solution and form uniform films with excellent quality, but their disordered, amorphous-like microstructures have intrinsically lower mobilities. The big question is therefore how to solution-process OSCs that exhibit high mobilities. Herein, this article provides an overview into the seemingly intrinsic trade-off between structure/solution-processing and electronic properties, and how this is defined within small-molecules and polymers. The article will finish with a brief discussion on an approach to overcome this trade-off, namely blending together small-molecules and polymers, as an all-round “best of both worlds” solution to the performance versus processing trade-off.

Background/Fundamentals: Organic Semiconductors

More than 70 years have passed since the initial investigations into electrical properties of organic compounds. Notable discoveries range from Pope *et al.*'s 1963 demonstration of electroluminescence in wide bandgap anthracene single crystals, to Shirakawa, Heeger, and MacDiarmid's Nobel Prize winning 1977 report on electrical conductivity in polyacetylene from doping post-treatments, to Burroughes, Bradley and Friend's polymer OLED in 1990.

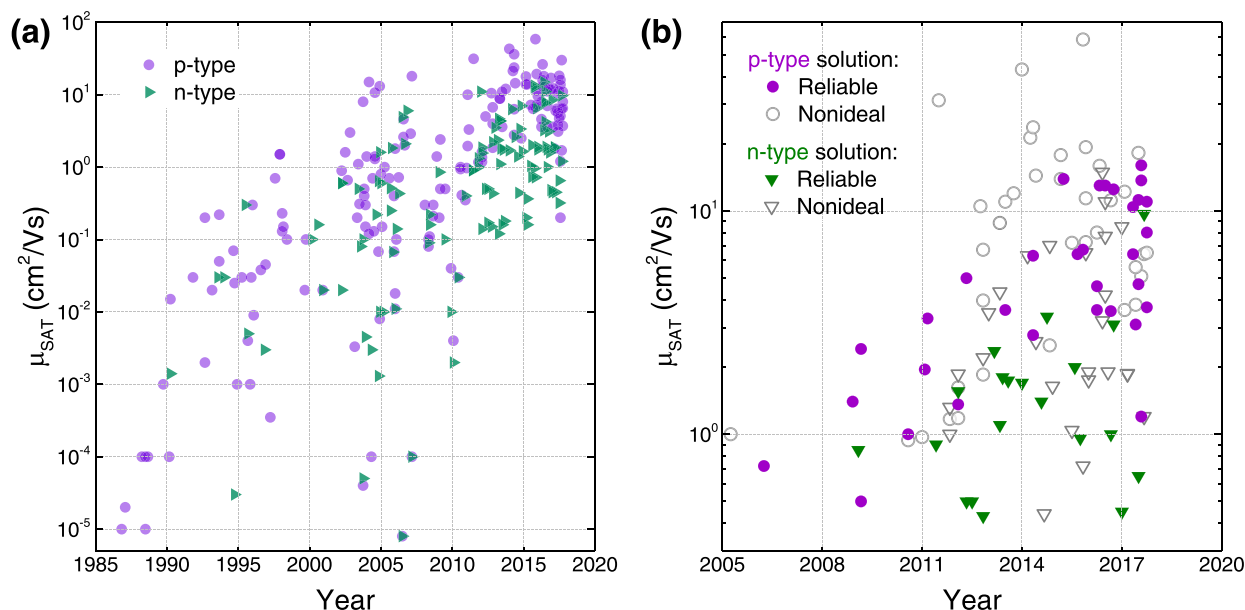


Fig. 2 Published mobilities measured in organic thin-film transistors, for p-type and n-type organic semiconductors, over the last three decades, from the late 1980s to 2018. In (b), this data has been “filtered” for features in the experimental OTFT data that do not comply with the classical field-effect transistor model. “Reliable” data has no obvious nonidealities. “Nonideal” covers data not shown; the kink/any s-shaped/nonlinear feature in $\sqrt{\text{drain current}}$ versus gate voltage; steepening $\sqrt{\text{drain current}}$, and non-saturated output characteristics). The graph in (b) suggests that 55% of data set shown in (a) has a nonideality or has not shown the data used to extract mobility. Reproduced with permissions from reference Paterson, A.F., *et al.*, 2018. Recent progress in high-mobility organic transistors: A reality check. *Advanced Materials* 30 (36), 1801079.

OSCs contain carbon. For plastics to behave as semiconductors, as opposed to household insulating polymers, the carbon unpaired electrons in two out of the three 2p orbitals must approach the full 2s orbitals of other carbon, in such a way that the 2s orbitals combines with two of the 2p orbitals (e.g., 2p_x and 2p_y). Otherwise known as sp² hybridization, the 2p_z orbital will remain as it was, whilst new, hybridized sp² orbitals are available to overlap with the sp² orbitals in another C atom in plane at 120°. This, in turn, forms in-phase and out-of-phase bonding (Ψ_{σ}) and antibonding (Ψ_{σ^*}) orbitals, with energies E_{σ} and E_{σ^*} respectively. Similarly, the 2p_z orbitals (that have not taken part in the sp² hybridization) overlap with each other to form a bonding (Ψ_{π}) and an antibonding orbital (Ψ_{π^*}). The latter is known as a π -bond, with the π -orbital contributing little to the attractive force between nuclei – unlike the σ -bond – as a result the overlapping electron density being further away from the internuclear axis. In addition to sp² hybridization, Peierls distortion is required to dimerize/stabilize the non-constant charge distribution. The latter results in alternating single and double bonds between neighboring carbon atoms, which causes further separation of the π -bond’s Ψ_{π} and Ψ_{π^*} orbitals. This is perceived as an energy gap analogous to that in inorganic semiconductors. In OSCs, the valence and conduction bands are termed HOMO (π) and LUMO (π^*). (Fig. 1).

For those materials that meet the criteria of both sp² hybridization and conjugation (i.e., alternating carbon single and double bonds), electronic charge carriers, holes or/and electrons, are transported between conjugated segments. How good or otherwise the π -overlap or π -stacking is between these conjugated groups therefore determines how efficiently the charges can travel/transport throughout the entire material. It follows that a material with better structural ordering will have better segment overlap, resulting in more efficient transport of holes and/or electrons. How efficiently charges transport through an OSC is commonly assessed using mobility, μ . μ is the velocity with which an electron (or hole) moves in response to an electric field:

$$\mu = \frac{v}{E} \quad (1)$$

where v is drift velocity (cm s⁻¹), E is electric field (V cm⁻¹), and μ has units (cm² V⁻¹ s⁻¹). OSC mobility is commonly measured using OTFTs. This is one of the many uses for OTFTs – they are significant and technologically fundamental in their own right, and deep OTFT analysis also provides insight into fundamental charge transport properties. In recent years it has been shown extensively that nuanced OTFT behaviors and parasitic effects need to be considered, when assessing OSC mobilities. Namely, reported OTFT mobility values can be overestimated if an OTFT suffers from contact resistance (resistance/Schottky barrier at the interface between the carrier injecting/extracting electrodes and the semiconductor), when it has a relatively low channel resistance (as with many higher mobility systems) (Choi *et al.*, 2018a; Bittle *et al.*, 2016; Uemura *et al.*, 2016). Even taking such data-based artifacts and mobility overestimations into account, the OTFT literature clearly shows that OSC mobilities have steadily and dramatically improved over the years (Fig. 2): from hole mobilities of 10⁻⁵ cm² V⁻¹ s⁻¹ (Tsumura *et al.*, 1986) in 1986, to accurately reported hole mobilities over 20 cm² V⁻¹ s⁻¹ in 2019, (Paterson *et al.*, 2019; Lampert *et al.*, 2018; Paterson *et al.*, 2018) We note from here that any

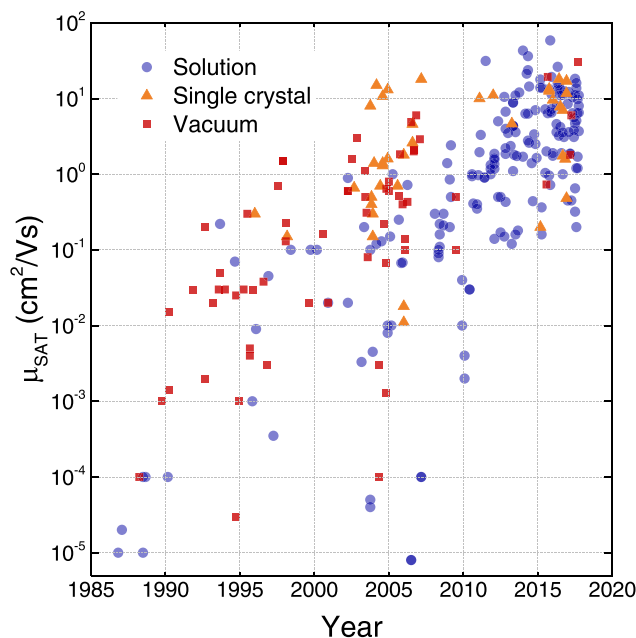


Fig. 3. Reported/published mobilities for organic semiconductors measured in organic thin-film transistors over the last three decades, from the late 1980s to 2018. The data set has been categorized by processing technique: solution processed, single crystal, and vacuum. It shows that historically, single crystal data and vacuum processed data has given the highest mobilities. However, solution-processed systems have made great improvement over the years; note the highest reported solution-processed mobility values shown on this figure are overestimated. Reproduced with permissions from reference Paterson, A.F., *et al.*, 2018. Recent progress in high-mobility organic transistors: A reality check. *Advanced Materials* 30 (36), 1801079.

mobility values quoted herein are used as a guide, and we refer the reader to the extensive literature covering the specifics of this topic (Choi *et al.*, 2018a; Bittle *et al.*, 2016; Waldrip *et al.*, 2020; Paterson *et al.*, 2018), Uemura *et al.* (2016).

Main Body

Another clear/consistent trend in this literature is that small-molecules overall have higher mobilities than polymers. Both small-molecules and polymers are highly soluble in a broad range of solvents, and are well-suited to the broad suite of OSC solution-processing techniques on offer, from spin-coating, to inkjet printing and gravure printing. For more information on the latter, Diao *et al* have written a comprehensive review detailing and categorizing solution-based processing techniques into drop casting, spin coating, printing, such as stamping or inkjet printing and meniscus guided coating techniques such as dip-coating, zone casting, hollow-pen writing, blading, solution shearing (Diao *et al.*, 2014).

Small-molecules are sp^2 hybridized, small, conjugated monomer systems, formed from chains or fused units of fundamental unsaturated building blocks, that are able to order themselves into crystals; small-molecules are also generally lighter and tend to have lower boiling points for easier purification via thermal evaporation. In highly ordered, crystalline regions (i.e., crystallites bordered by grain boundaries), there is better π -stacking or overlap between conjugated sections. This results in better transport and therefore higher mobilities. On the other hand, polymers are large molecules, with long chains comprising multiple simpler, repeating monomer subunits. The size of the polymer chain is defined by the number of repeating monomers in the chain. They are much greater in size than small-molecules, typically form amorphous or amorphous-like structures, and continuously change along their length. The continual changes along their long lengths lead to disruptions in conjugation, a higher level of disorder, and less overlap between ordered sections. Although well-ordered, larger crystals can be obtained from small molecules versus polymers – where the crystal domains are typically much smaller – polymers possess have better mechanical compliance for large-area processing and solution processability because of their long polymer chains (Kymissis, 2009). Overall, small-molecules have preferential structures for higher mobilities, yet it's different to obtain these structures via solution-processing. Polymers have structures counterintuitive to high mobilities, yet they are easily to process from solution. The general mobility trends and corresponding structural differences between the two material families highlight the impact of crystallinity/disorder on charge transport/mobility, as well as the material-processing-mobility relationship Fig. 3.

Small-Molecules

Band-like charge transport occurs in well-ordered, periodic crystal structures (e.g., single crystal silicon) and crystalline regions. In periodic structures, charge carriers are considered in potential wells within periodic boundary conditions. Solving the Schrodinger

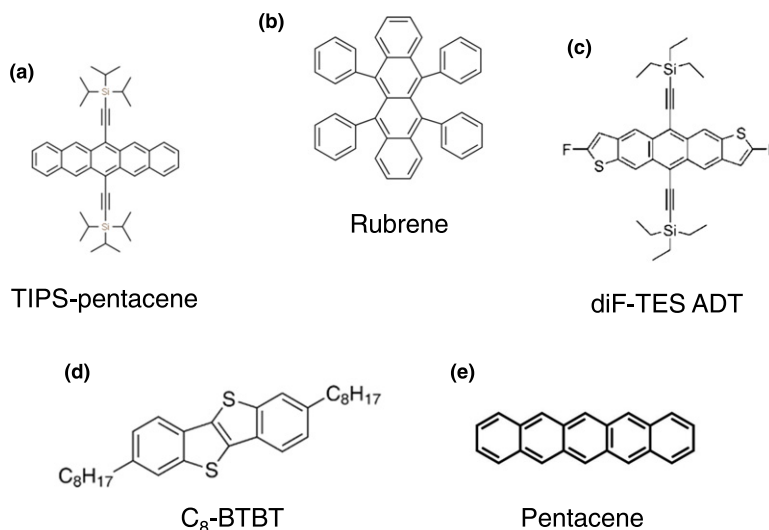


Fig. 4. Examples of small-molecules: (a) 6,13-bis(triisopropylsilyl)ethynylpentacene (TIPS-pentacene), (b) 5,6,11,12-tetraphenyltetracene (rubrene), (c) 2,8-difluoro-5,11-bis(triethylsilyl)ethynylanthradithiophene (diF-TES ADT), (d) 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C₈-BTBT), and (e) pentacene.

equation within periodic boundary conditions gives an energy distribution in two periodic bands, with no solution to the Schrodinger equation in the bandgap. The wavefunctions and therefore electrons are delocalized throughout the bands.

It follows that ordered crystallites enable efficient charge transport. Generally, mobility can be increased by extending both the intramolecular and intermolecular π - π conjugation; increasing the aromatic rings help with the former, and crystal packing affects the latter. The importance of molecular packing on charge transport is shown clearly in a study by Rovira *et al.* in which large measured mobility variation, from 10^{-5} to $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, was observed as a function of packing in the case of single tetrathiafulvalene crystals, (Moon *et al.*, 2004; Coropceanu *et al.*, 2007). A layered herringbone crystal packing is typically favorable for most unsubstituted π -conjugated molecules, because it provides 2D charge transport within the layers while the interlayer transport is less efficient. However, herringbone packing with a combination of face-to-face and edge-to-face molecular interactions yields limited charge transport due to poor intermolecular interactions between adjacent molecules along the herringbone diagonal. To overcome this hinderance, Anthony and co-workers developed a new approach for derivatization of conjugated backbone in such a way that the preferred crystal structure is no longer edge-to-face molecular interactions but rather face-to-face (Anthony, 2006) (Fig. 4).

Charge carrier transportation is also inhibited (trapped) by the disordered grain boundaries (Rivnay *et al.*, 2009; Smith *et al.*, 2010b). Therefore, if an OSC has a higher propensity to crystallize, it will have a higher mobility, as long as the energetic conditions/terms applied to it (i.e., processing) are favorable for the formation of large crystals, where larger crystals are typically associated with higher mobilities (Horowitz and Hajlaoui, 2001) (although we note that in practice, this is not always the case). However, achieving such large crystallites with solution-processing is non-trivial, because small-molecule crystallization kinetics are difficult to control whilst the solvent is evaporating. It is therefore challenging to form neat layers, or large crystallites with low numbers of defect-filled grain boundaries (i.e., charge trapping sites). For this reason, some of the highest OTFT/OSC mobilities reported to-date are for small-molecules fabricated via vacuum sublimation, under controlled conditions, (Jurcescu *et al.*, 2004; Hu *et al.*, 2021) Although this fabrication approach helps with material purification, whilst enabling highly ordered crystalline layers, the lack of simplicity and complicated instrument requirements mean this method does not fit with the long-term vision of low cost, large area, solution-processed plastic electronics. The ability to process highly crystalline small-molecule OSCs, from solution and under ambient conditions, is therefore highly desirable for plastic electronic device fabrication.

For example, one of the most well-studied small-molecule OSCs is pentacene. Pentacene tends to form crystalline domains, that subsequently have high mobilities. However, the main drawback of pentacene is its insolubility in many organic solvents, making costly vacuum deposition its most viable fabrication process (Gundlach *et al.*, 1997). A common approach for solubilization is to introduce bulky side groups to the backbone of the molecule. Although these side groups can disturb ideal packing motifs, molecular engineering studies show that suitable side groups can actually enhance molecular packing, subsequently increasing charge carrier mobility. For instance, TIPS-pentacene is a functionalized pentacene derivative, where solid-state ordering is controlled such that significant improvements in electronic properties are observed, in addition to solubility in most organic solvents (Anthony, 2006). Other materials, such as 5,11-bis(triethylsilyl)ethynyl anthradithiophene (TES-ADTs), is built around an ADT molecular backbone with good electronic performance and limited solubility. Whilst adding bulky TES side groups enhances solubility, it simultaneously reduces the solid-state ordering by limiting intermolecular interactions, and typically results in amorphous films (Chen *et al.*, 2014). This barrier was overcome by synthesis of fluorinated ADT (diF-TES ADT) that demonstrates enhanced crystallinity from the F-H and F-S interactions between adjacent molecules (Lee *et al.*, 2009).

Another challenging aspect of solution-processing small-molecules, is they can adopt different molecular arrangements, leading to the formation of polymorphs. The same OSC material subsequently exhibits different optoelectronic properties and device

performance, arising from the different polymorphic structures (Yu *et al.*, 2021). Controlling the morphology of small-molecule OSCs during solution deposition therefore plays a crucial role in device performance and mobilities measured in OTFTs, (Lim *et al.*, 2009; Virkar *et al.*, 2010; Hiszpanski and Loo, 2014). Developing methods to control morphology during solution processing has therefore been a key area of research interest, (Diao *et al.*, 2013; Lee *et al.*, 2009; Nakayama *et al.*, 2011). Giri *et al.* used a lattice strain technique to alter the π - π stacking distance in TIPS-pentacene transistors, which increased hole mobility from $0.8 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in unstrained films, to $4.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in strained films (Giri *et al.*, 2011). Minemawari and coworkers developed a method combining antisolvent crystallization and inkjet printing, to produce highly crystalline C₈-BTBT films, yielding OTFTs with an average mobility of $16.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (Minemawari *et al.*, 2011). Vapor annealing amorphous TES-ADT films has also been shown to change active layer OSC morphology and mobility; for instance, using this approach to enable TES-ADT crystallization improved mobility from $0.002 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (amorphous films) to $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (crystallinity films) (Dickey *et al.*, 2006). Thermal annealing can also be used to encourage molecular motion and subsequently crystallize small-molecules. The latter has been shown to improve mobility by more than a factor of two in pentacene OTFTs (Lee and Loo, 2010).

Several high-performance, air-stable small-molecules have been developed with (Anna Köhler, 2015) benzothieno[3,2-*b*] (Anna Köhler, 2015)- benzothiophene (BTBT) as their core structure, for vacuum processed OSCs. The molecular overlap can be enhanced by adding alkyl groups to the BTBT core structure in C_n-BTBTs, which exhibit superior charge transport properties. Alkylated BTBTs have better solubility. This solubility doesn't increase monotonically with elongation of the alkyl chain, however; it peaks for C₉H₁₉ and then reduces for derivatives with alkyl groups longer than C₁₂H₂₅. Although those with longer alkyl chains (C_n > 8) have herringbone packing, that brings sulfur atoms adjacent to the BTBT cores closer, and results in stronger intermolecular charge transfer, their films typically suffer from lower quality and therefore less electron-phonon coupling and reduction in mobilities (Wawrzinek *et al.*, 2019). Amongst all the alkylated derivatives, C₈-BTBT is the most widely used and commercially available due to its relatively larger mobility, solubility and higher film quality, (Ebata *et al.*, 2007; Wawrzinek *et al.*, 2019; Izawa *et al.*, 2008).

Polymers

Like small-molecules, the electronic properties of polymer OSCs are governed by conjugation and π - π stacking. In contrast to small-molecules, polymers form excellent quality, uniform thin-films when processed from solution, and exhibit greater flexibility and foldability, because of their long molecular chains and subsequent, predominantly amorphous characteristics. Larger molecular conjugation networks typically result in smaller HOMO-LUMO band gaps, with dimerization preventing polymers with nearly infinite conjugation networks (compared to small molecules) from having no band gap (Kymissis, 2009). Smaller band gaps are, in themselves, advantageous for OSC applications. However, polymer mobilities are limited by their inherent energetic disorder. Charge transport occurs in highly disorder amorphous regions; conjugated segments vary considerably in length, which leads to bandgap energy variations and increase disorder. The π -electrons are delocalized within conjugated segments, rather than across a whole system – in contrast to band-like transport – and in such disordered systems, charge transport is considered as hopping between discrete sites. The widely accepted description for charge transport through disordered polymers is “hopping” through a series of localized states. This charge transport can be enhanced by addressing and improving the disordered microstructure. For example, one of the most widely studied OSCs, semicrystalline regioregular poly(3-hexylthiophene) (P3HT), benefits from a lamellar structure that self-organizes into 2D charge transport pathways (Wang *et al.*, 2017). When the polymer thin-film adopts an edge-on backbone orientation relative to the substrate, it will have a higher mobility ($0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) (Sirringhaus *et al.*, 1999).

Microstructure can be tailored/enhanced via chemical synthesis, fabrication techniques, or a combination of both. One approach for chemical synthesis, having significant impact on effective conjugation length, is side-chain engineering; carefully considering side chain geometry and positioning can maximize polymer electronic performance, (Kline *et al.*, 2007; Fei *et al.*, 2014). Approaching the topic of chemical synthesis over the years has resulted in the development of more complex synthetic procedures and new polymer families introduced. Long-range order and edge-on orientations, as with P3HT, are now no longer critical for achieving high charge carrier mobilities. Introducing fused building blocks with rigid aromatic monomer units and extended π -conjugation (Paterson *et al.*, 2018) results in polymers with high performance governed by unusual rigidity and low energetic disorder along the conjugated backbone (Liu *et al.*, 2008). One of the most notable polymers exhibiting this characteristic is indacenodithiophene (IDT). Copolymerizing the IDT unit with electron deficient 2,1,3-benzothiadiazole (BT), along with careful modification of the alkyl side chains, enhances the mobility from 0.15 to $1.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in this copolymer (Bronstein *et al.*, 2011). Increasing IDT-BT molecular weight further increases mobility, with C₁₆IDT-BT achieving remarkable hole mobilities of up to $3.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Although C₁₆IDT-BT films exhibit amorphous and poorly order microstructures, the high mobility (Zhang *et al.*, 2013) suggests long-conjugated polymer chains are primarily responsible for charge transport through poorly ordered semiconducting polymers, where electrical pathways are between amorphous and polymer aggregated regions within the film.

In terms of fabrication techniques to enhance charge transport properties, both crystalline domains in semicrystalline materials (grain size and orientation, degree of crystallinity) as well as amorphous domains (chain alignment and orientation, tie chain density), must be controlled in the resultant film morphology. A broad range of solution-processing techniques are employed for polymer deposition. On one hand is spin-coating; this is the most utilized, simple and available technique for lab-scale research, but controlling thin-film morphology is extremely difficult, because there is no shear stress applied uniformly whilst coating takes place. On the other hand, meniscus-guided coating techniques, such as dip coating, blade coating, solution shearing, and slot die coating, can overcome such concerns: film deposition is guided and controlling by a non-contact coating head or viscous forces translating a meniscus across a substrate (i.e., printing head not in physical contact with the substrate) (Gu *et al.*, 2018). Similarly,

Table 1 Summary of small-molecule versus polymer reported mobility values and their relationship with solution-processing

Material	Type		Reported μ_{sat} ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Processing technique	Dielectric	Year	References
	Small-mol.	Polymer					
Pentacene	✓		40	Physical vapor deposition	PQ	2007	Jurchescu <i>et al.</i> (2007)
TIPS-pentacene	✓		(a) 2.4	(a) Slot die coating	(a) PMMA	(a) 2018	Lin <i>et al.</i> (2018), Diao <i>et al.</i> , (2013)
			(b) 11	(b) Modified solution shearing	(b) PTS-modified SiO ₂	(b) 2013	
diF- TES ADT	✓		(c) 19.2	(c) Spin cast	(c) SiO ₂	(c) 2018	Lamport <i>et al.</i> (2018)
C ₈ -BTBT	✓		(a) 6.5	(a) Spin cast	(a) SiO ₂	(a) 2017	Wei <i>et al.</i> (2017), Liu <i>et al.</i> (2017),
			(b) 13	(b) Drop casting	(b) CYTOP + Parylene C	(b) 2017	Minemawari <i>et al.</i> (2011)
			(c) 31.3	(c) Ink-jet printing	(c) Parylene C	(c) 2011	
C ₁₀ DNTT	✓		11	Controlled solution-crystallized	SiO ₂	2011	Nakayama <i>et al.</i> (2011)
C ₁₃ -BTBT	✓		17.2	Thermal evaporation	AlO _x	2012	Amin <i>et al.</i> (2012)
4CL-TAP	✓		27.8	Dip-coating	CDPA-AlO _x /SiO ₂	2018	Chu <i>et al.</i> (2018)
C ₆₀	✓		11	Droplet-pinned crystallization (DPC)	BCB covered SiO ₂	2012	Li <i>et al.</i> (2012)
DT-TTF	✓		3.65	Drop casting	SiO ₂	2008	Leufgen <i>et al.</i> (2008)
DB-TTF	✓		0.5	Drop casting	SiO ₂	2008	Leufgen <i>et al.</i> (2008)
DPh-DNTT	✓		3.6	Thermal sublimation	TDPA-AlO _x	2020	Borchert <i>et al.</i> (2020)
P3HT		✓	0.1	Spin cast	SiO ₂	1999	Sirringhaus <i>et al.</i> (1999)
IDT-BT		✓	1.2	Spin cast	CYTOP	2011	Bronstein <i>et al.</i> (2011)
C ₁₆ IDT-BT		✓	3.6	Spin cast	CYTOP	2013	Zhang <i>et al.</i> (2013)
PNDIF-T2		✓	6.5	Spin cast	SiO ₂	2016	Kang <i>et al.</i> (2016)
PDBPyBT		✓	6.3	Spin cast	SiO ₂	2014	Sun <i>et al.</i> (2014)
FBDPPV-1		✓	1.7	Spin cast	CYTOP	2015	Lei <i>et al.</i> (2014)
DPP-DTT		✓	1.5	Spin cast	ODTS/SiO ₂	2021	Ghamari <i>et al.</i> (2021)
P-29-DPPDTSE		✓	12.04	Spin cast	OTS/SiO ₂	2013	Kang <i>et al.</i> (2013)
DPA		✓	34	Physical vapor transport	OTS/SiO ₂	2015	Liu <i>et al.</i> (2015)

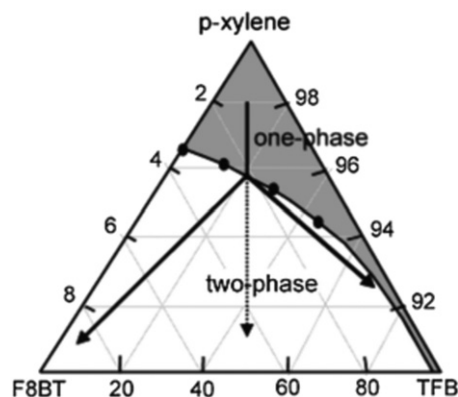


Fig. 5 Ternary phase diagram, for poly(9,9-dialkylfluorene-alt-triarylamine) (TFB) and poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) and solvent (p-xylene). It shows the phase separation and solvent evaporation processes at 22°C. Reproduced with permission from reference Smith, J., *et al.*, 2010a. Solution-processed organic transistors based on semiconducting blends. *Journal of Materials Chemistry* 20 (13), 2562–2574.

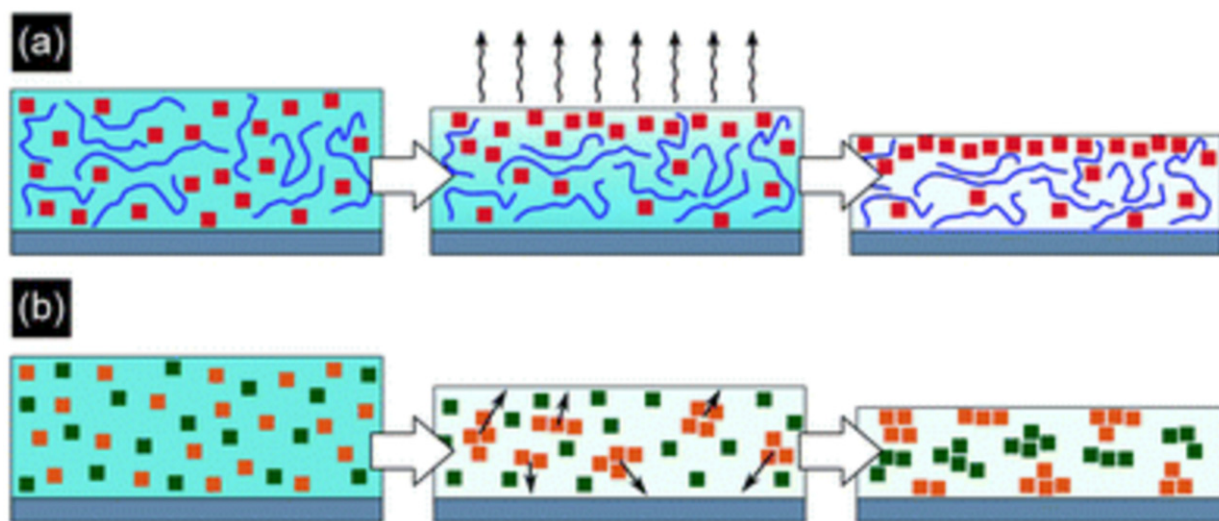


Fig. 6. Typical vertical phase separation in small-molecule/polymer blends. (a) Solvent evaporation causes a concentration gradient, with the more soluble material migrating to the surface/air interface (red squares). (b) The material that crystallizes first in the order determines the microstructure, in phase separation induced by crystallization; here, orange squares crystallize first, and, as the green squares crystallize, they are expelled to the interface. Reproduced with permission from reference Smith, J., *et al.*, 2010a. Solution-processed organic transistors based on semiconducting blends. *Journal of Materials Chemistry* 20 (13), 2562–2574.

aligning conjugated polymer backbones uniaxially can be achieved via post-deposition techniques, such as mechanical rubbing and stretching, or via slow/unidirectional drying under capillary action within prepatterned grooves, or confined structures. These are effective, laboratory scale techniques for producing highly aligned films that maximize intramolecular overlap and subsequently improve charge transport. Finally, single step deposition techniques such as zone casting, shear coating, slot-die coating (on patterned substrates) and wire-bar coating have been shown to induce shear stresses that produce highly aligned, anisotropic films, with high measured mobilities in the alignment direction (Khim *et al.*, 2018) **Table 1**.

Small-Molecule/Polymer Blends

There is one approach that overcomes the small-molecule versus polymer conundrum, to balance solution-processing with electronic performance. Namely, blending the two material types together to produce a “best of both worlds” system in a single OSC layer. In other words, combining the film-forming qualities from the polymer, with the high mobilities from the small-molecule. The concept was originally introduced as patents, and for more than a decade since, the research led by Professor Thomas D. Anthopoulos has consistently shown that small-molecule/polymer blends are some of the highest mobility solution-processed OSCs, as measured in OTFTs, (Paterson *et al.*, 2019; Hamilton *et al.*, 2009; Smith *et al.*, 2012; Paterson *et al.*, 2016).

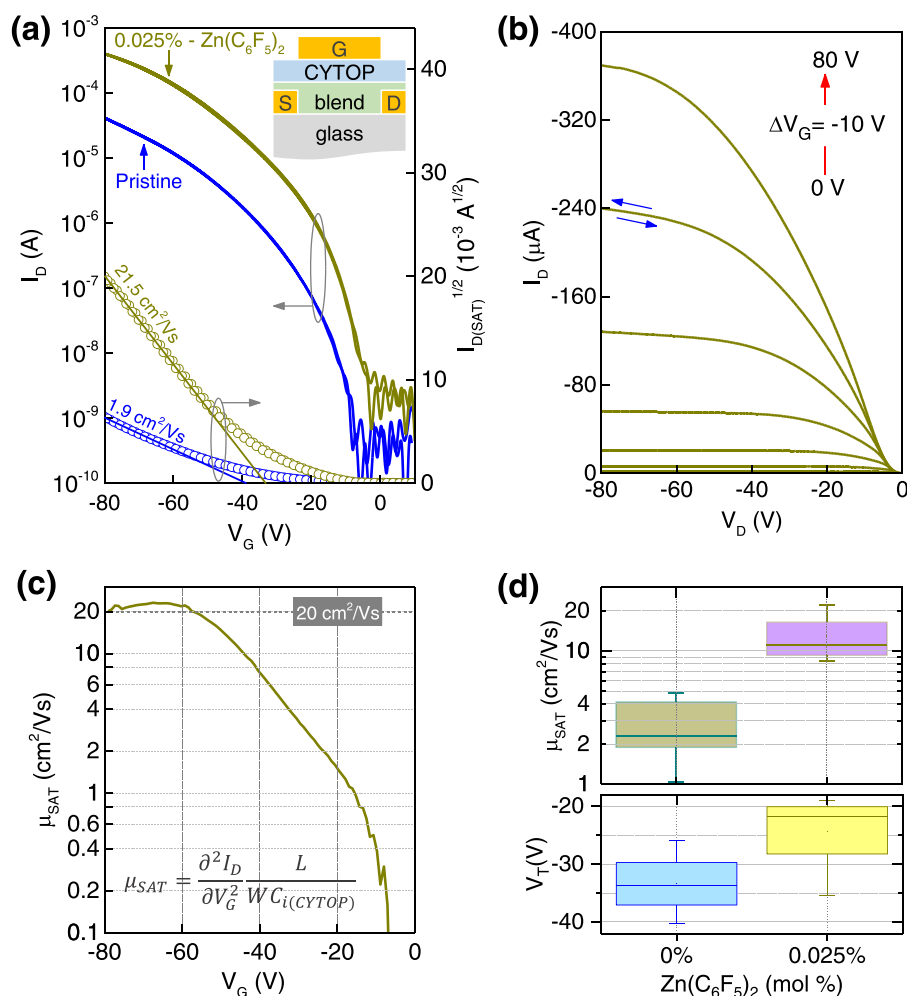


Fig. 7 OTFT characteristics for a ternary blend of C₈-BTBT:C₁₆IDT-BT:Zn(C₆F₅)₂. (a) Transfer curves showing the impact of the Zn(C₆F₅)₂ dopant on small-molecule/polymer blend mobility. (b) Output curve for best-performing ternary blend composition. (c) Second derivative. (d) Statistics from 12 OTFTs, for saturation mobility and threshold voltage, show the impact of the dopant in the small-molecule/polymer. Reproduced with permission from reference Paterson, A.F., *et al.*, 2019. Addition of the lewis acid Zn(C₆F₅)₂ enables organic transistors with a maximum hole mobility in excess of 20 cm²V⁻¹s⁻¹. *Advanced Materials* 31 (27), 1900871.

One of the key benefits of the small-molecule/polymer blends, is the versatile, broad range of microstructures they offer, compared to a single-material system. A critical aspect of the final blend microstructure is how the small-molecule and polymer phase separate during solution-processing and solvent evaporation. Their phase separation can more generally be predicted by constructing phase diagrams, that consider all three components: the polymer, small-molecule and the solvent. Typically, a small-molecule/polymer blends deposited from the solution-phase will undergo liquid-liquid phase separation. There are two routes by which this can happen: (1) spinodal decomposition, and (2) nucleation and growth (Smith *et al.*, 2010a; Zhao *et al.*, 2016). The former spinodal decomposition case is a spontaneous process that occurs as a result of the blend component miscibility, and is a common mechanism for phase separation of polymer/polymer blends. Nucleation and growth, on the other hand, is determined by the component that nucleates first and is the dominant mechanism for small-molecule/polymer blends, where the highly crystalline small-molecule nucleates first. This occurs homogeneously, with nuclei spontaneously appearing in a meta-stable state, or heterogeneously, with the new phase appearing on a surface or at impurity particles. For a small-molecule/polymer/solvent mixture, as the solution becomes supersaturated by, for example, a change in solution concentration (solvent evaporation) or temperature, the small-molecule component tends to nucleate at the surface/air interface (Fig. 5).

In the case of small-molecule/polymer blend, nucleation and growth usually results in vertical phase separation, i.e., a layer of small-molecule on top of a layer of polymer. This happens because nucleation drives solidification, via a change in Gibbs free energy, creating smooth, solid-liquid interfaces advance as lateral ledges, growing as a result of the surface nucleation (Patrick Augustijns, 2007; Sunagawa, 2005). In contrast to a neat small-molecule deposited as a solution, the polymer binder affectively aids the formation of a small-molecule thin-film, reduces nucleation rates and slows/controls growth processes, without the need for additional, complex or expensive fabrication techniques. This leads to large crystallites with reduced grain boundaries, and this improved morphology results in high mobilities

reference (Smith *et al.*, 2010a). Overall, there are many variables that impact how the small-molecule nucleate in the blend, and therefore many variables that influence the final blend morphology, subsequently dictating its electronic properties: small-molecule and polymer chemical structures, polymer molecular weight, solvent choice (including “bad” solvents), temperature treatment, surface tension/treatment and wetting on the substrate, miscibility between materials, degree of polymer crystallinity, solvent evaporation rate, blend ratios, diffusivity, choice of fabrication technique and solution concentration/viscosity (Cho *et al.*, 2013; Liu *et al.*, 2009) Fig. 6.

However, the polymer plays a more critical role that simply aiding small-molecule crystallization, increasing its crystallite size and reducing grain boundary density. An important aspect of small-molecule/polymer blend is the critical and active role the polymer plays; namely, the intrinsic performance and energy levels of a semiconducting polymer is of the utmost importance. From extensive small-molecule/polymer blend research over the years, there are specific stand-out criteria for blend design, resulting in sequential steps for improving mobility:

Small-molecule blended with an insulating polymer binder

Blending a small molecule with an insulating polymer binder will improve film forming properties, and hence electrical performance, when comparing a neat small-molecule counterpart processed under the same conditions. Originally it was thought that such an approach with an insulating binder would “dilute” the high mobility of the small-molecule. However, the characteristic vertical phase separation has since been found to routinely enhance the small-molecule formation in such a way that mobility is improved (Smith *et al.*, 2010b).

Small-molecule blended with a semiconducting polymer binder

Using a semiconducting polymer binder, as a replacement for the insulating polymer binder, will increase mobility of the blend in like-for-like processed systems. Some key criteria must first be satisfied, for example, energy level matching between the small-molecule and the polymer. In 2009, Hamilton *et al.* used this approach to achieve record breaking solution-processed hole mobility values of $\mu_{\text{sat}} = 2.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with a blend of diF-TES ADT with semiconducting poly(triarylamine (PTAA), compared to a blend with diF-TES ADT with insulating poly(α -methylstyrene) (PzMS) (Hamilton *et al.*, 2009).

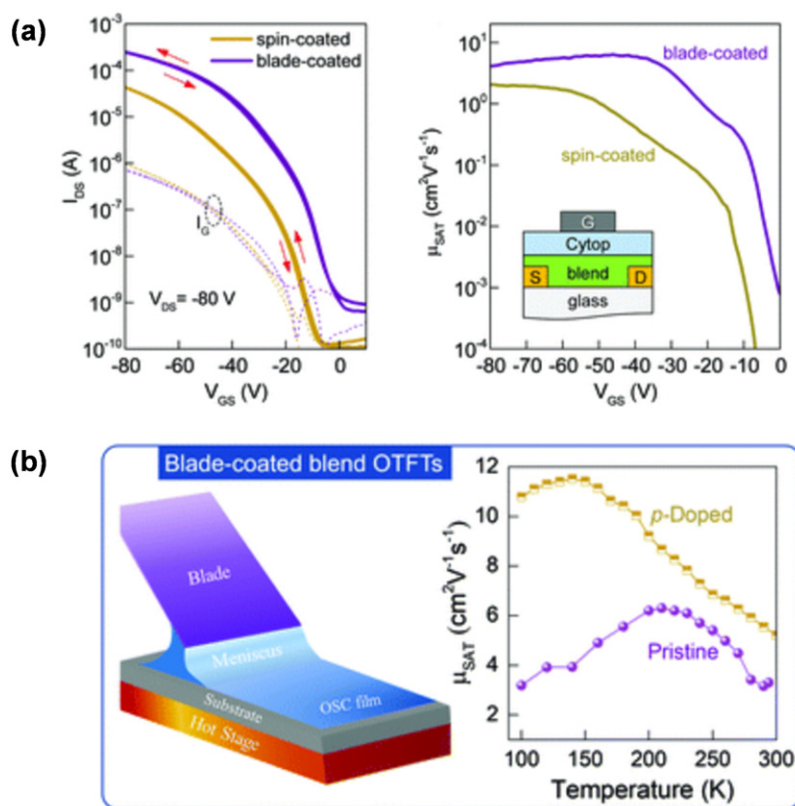


Fig. 8 Impact of different solution-processing techniques on ternary blend made with C₈-BTBT:C₁₆IDT-BT:C₆₀F₄₈. (a) Representative transfer characteristics and saturation mobility plots versus gate voltage, for spin-coated versus blade coated ternary blend OTFTs. (b) Overview of the impact blade coating ternary blend has on mobility over temperatures to study the impact of doping on charge transport. Reproduced with permission from reference Basu, A., *et al.*, 2020. Impact of p-type doping on charge transport in blade-coated small-molecule:polymer blend transistors. Journal of Materials Chemistry C 8 (43), 15368–15376.

Small-molecule blended with a high mobility semiconducting polymer binder

Exchanging the semiconducting polymer binder for a semiconducting polymer with higher mobility further increases the mobility of the blend. Smith *et al.* showed this in 2012, by changing the aforementioned polymer binder (PTAA) to an even higher performing semiconducting polymer binder, poly(dioctylfluorene-co-bis-N,N'(2,4-dimethylphenyl) diphenylaminodimethyl) (PF-TAA), (Smith *et al.*, 2012; Su *et al.*, 2012) and more than doubling the mobility (to $> 5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).

Conductive atomic force microscopy (C-AFM) has shown that part of this effect is caused by extremely low resistance grain boundaries, in blends containing semiconducting polymer binders, compared to neat small-molecule films and small-molecule/polymer blends with insulating binders (Hunter and Anthopoulos, 2013). The latter suggests mixed-phase small-molecule/polymer grain boundaries promote intergrain connectivity, enhancing carrier transport between high mobility domains. This is most likely caused by the vertical phase separation.

Ternary blend: Adding a dopant to a small-molecule blended with a high mobility semiconducting polymer binder

Adding a molecular dopant into a small-molecule/polymer blend produces a ternary blend system with even further increase in mobility and reduced energetic disorder (Iurchescu, 2021). In 2016 Paterson *et al.* added the fluorofullerene, $\text{C}_{60}\text{F}_{48}$, as a molecular dopant into a small-molecule/polymer blend of $\text{C}_8\text{-BTBT}$ and $\text{C}_{16}\text{IDT-BT}$, and achieved maximum spin-coated hole mobilities of $13 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ —significantly higher than individual spin-coated components ($\text{C}_8\text{-BTBT}$, $2.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$; $\text{C}_{16}\text{IDT-BT}$, $3.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) (Paterson *et al.*, 2016). For over 50 OTFTs, the average mobility improvement from 1.4 to $7.8 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with and without dopant, respectively (Paterson *et al.*, 2017). Choi *et al.* showed bandlike transport occurs in this ternary blend systems (Choi *et al.*, 2020; Choi *et al.*, 2018b). Scaccabarozzi *et al.* recently showed the ternary blend composition itself dictates thermally activated or band-like charge transport behavior. Charge-modulation spectroscopy showed that, without the dopant, holes relax onto the conjugated polymer where shallow traps dominate carrier transport. On the other hand, in the doped system, the $\text{C}_{60}\text{F}_{48}$ deactivates the shallow traps and this enables better hole delocalization in the vertically phase separated $\text{C}_8\text{-BTBT}$ upper layer, causing high mobilities (Scaccabarozzi *et al.*, 2020) (Fig. 7).

In 2018, Panidi *et al.* (2018) used the Lewis acid tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) as a dopant for blends of TIPS-pentacene:PTAA, diF-TES ADT:PTAA and $\text{C}_8\text{-BTBT}:\text{C}_{16}\text{IDT-BT}$, and achieved maximum mobilities of 3.7, 8, and $11 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. Paterson *et al.* used a different Lewis acid, bis(pentafluorophenyl)zinc ($\text{Zn}(\text{C}_6\text{F}_5)_2$), to obtain extremely high hole mobilities of $21.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, in $\text{C}_8\text{-BTBT}:\text{C}_{16}\text{IDT-BT}:\text{Zn}(\text{C}_6\text{F}_5)_2$ ternary blend OTFTs (Paterson *et al.*, 2019). In both cases, the Lewis acids were shown to act simultaneously as a *p*-dopant and a microstructure modifier, where $\text{B}(\text{C}_6\text{F}_5)_3$ promoted single-crystal-like long-range crystallinity in the small-molecule/surface morphology in the blend (Fig. 8).

Finally, it's worth noting that techniques other than spin coating can be employed for further control over small-molecule/polymer blend morphology. For example, Soeda *et al.* used continuous growth edge-casting method to produce solution-processed single-crystal OTFTs from a 3,11-didecylidnaptho[2,3-d:2',3'-d']benzo[1,2-b:4,5-b']dithiophene ($\text{C}_{10}\text{-DNBDT-NW}$):poly(methyl methacrylate) (PMMA), achieving maximum mobilities of $17 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (Soeda *et al.*, 2016). This mobility higher than the $\text{C}_{10}\text{-DNBDT-NW}$ alone and processed in the same way. Similarly, blade coating has shown excellent results on both binary and ternary blend systems with semiconducting binders. Niazi *et al.* found that blend nucleation and growth processes are different in blade coating than spin coating using diF-TES ADT and TIPS-pentacene-based blends (Niazi *et al.*, 2015a). Capitalizing on this, they demonstrate diF-TES ADT:polystyrene blend OTFTs with the same mobility as single-crystal diF-TES ADT OTFTs (Niazi *et al.*, 2015b). In a doped ternary blend of $\text{C}_8\text{BTBT}:\text{C}_{16}\text{IDT-BT}:\text{C}_{60}\text{F}_{48}$, Basu *et al.* showed that operating characteristics of blade-coated transistors consistently outperform spin-coated OTFTs, with maximum hole mobility $14 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and all-round improved operating characteristics (Basu *et al.*, 2020).

Conclusion

Overall, there are two clear trends for small-molecules versus polymers. The excellent propensity of small-molecules to crystallize makes them high mobility materials, whilst simultaneously making them difficult to control during solution-processing. Polymers, on the other hand, have excellent film-forming qualities because of their long chains, which simultaneously introduce intrinsic disorder and subsequently lower mobilities. This is important because, the better the electronic performance (or higher the mobility), the broader the market of possible OSC commercial applications. For the latter, the highest mobility OSCs are vacuum deposited small-molecules. However, one of the key goals of plastic electronics is large-area, low cost (non-batch) processing from solution. Therefore, over the years, a variety of techniques have therefore been researched, developed, and employed to overcome the small-molecule versus polymer trade-off between performance and solution-processability. For example, synthetic techniques such as side chain engineering, fabrication techniques that apply uniaxial shear stresses, or approaches that simply blend small-molecules and polymers together to produce a single system that is the best of both worlds. As time goes by and the plastic electronics field matures even further, small-molecules are better suited for exhibiting their higher mobilities whilst being compatible with simple solution-processing techniques. Similarly, polymer design strategies are developed that no longer rely on previous criteria, such as long-range order, for achieving high mobilities. Although there will always be some sort of trade-off for the neat material systems, other techniques, such as blending, combine the best properties from each material family. As techniques such as these continue to improve with ongoing research, it is expected that a point will be reached whereby we are no longer limited by the small-molecule versus polymer trade-off.

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Solution processed organic thin-film transistor for diplays and sensors

Xiaojun Guo, Lei Han, and Bang Ouyang, Department of Electronic Engineering Shanghai Jiao Tong University, Shanghai, China

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Abstract

Despite technological merits and promising application demands of solution processed organic thin-film transistors (OTFTs), there is still a gap to be filled for this technology to be commercially adopted. This paper will focus on suitable device structures and process methods for OTFT integration, which is key to bridge the intensive material research and the envisioned applications. The real advantages of solution processed OTFTs from the perspective of manufacturing and application will also be discussed. Then development of displays and sensors based on OTFTs will be reviewed. Finally, the challenges to be further addressed for solution processed OTFTs will be envisioned.

Introduction

(Number the main sections of the contribution) Provide an up-to-date and well-focused literature review stating the main and specific objectives of the contribution in this section.

The thin-film transistor (TFT) technologies have been key enablers for modern high information-content semiconductor displays by realizing active-matrix addressing backplanes [Nathan et al. \(2013\)](#). TFT backplane technologies based on hydrogenated amorphous silicon (a-Si:H), low temperature polycrystalline (LTPS) and amorphous metal oxide semiconductor (AOS), have been well established in industry to meet requirements for various main-stream display applications in performance, panel size and cost ([Brotherton 2013](#)). To meet the ever-increasing demands, but at lower manufacturing cost, the industry is exploring the capability limits of existing TFT technologies. The continuous technical advances of TFTs, also enable to extend TFT applications from pixel switches and current drivers to more complex electronic functions for general signal processing, data storage and computing.

On the other hand, TFTs of new material and processing technologies also attract great attention from both academia and industry for specific device performance enhancement, reduction of processing temperature and carbon emission, and new function integration ([Shim et al., 2020](#)). Compared to the inorganic counterparts, the organic thin-film transistor (OTFT) with solution processed organic semiconductor (OSC) and dielectric layers own advantages of low processing temperature, cost-effective manufacturing and excellent mechanical flexibility ([Guo et al. \(2017\)](#)). Therefore, it has attracted wide research attention for making flexible or stretchable electronics at low cost and energy consumption. In the last decade, the reported mobility values of OSCs in literature have remarkably increased over several orders, indicating great promise for continuous performance improvement through material tailoring and process optimization ([Henson et al. 2012](#); [Sun et al., 2019](#)). These advances in materials and process techniques enabled using OTFTs to implement active-matrix display/backplanes, and various integrated circuits and systems ([Cain 2018](#); [Feng et al., 2018](#); [Hou et al., 2022](#)). However, despite both technological advances and promising application demands, there is still a gap to be filled for the OTFT technology to be commercially adopted.

There have been several review papers in the literature well covering the material development for solution processed OTFTs, including OSCs, gate insulator layer, buffer, surface treatment and encapsulation materials ([Schweicher et al., 2020](#); [Guo et al., 2021](#)). In OTFTs, the OSC channel accommodates carrier transport, and is the most key part affecting the device performance. The gate insulator (GI) layer, sandwiched between the gate electrode and the OSC layer, not only serves the barrier suppressing the gate leakage, but also affects the gate modulation capability of the channel. Besides the OSC and GI layers, stacking materials of the buffer, electrode treatment materials and encapsulation are also important for constructing OTFT devices and circuits.

This paper will focus on device structure and processing for integration, which is key to form solid link between the intensive material research and the envisioned applications. The real advantages of solution processed OTFTs from the perspective of manufacturing and application will also be analyzed. Then development of displays and sensors based on OTFTs will be reviewed. Finally, the challenges to be further addressed for solution processed OTFTs will be discussed.

Device Structures and Processes for Integration

Provide further background information (when applicable) and fundamentals related to the specific contribution here. This section might include sub-sections.

Device Structures

To fabricate a TFT, four possible structures as shown in [Fig. 1](#) can be used, depending on the sequences of depositing the gate electrode, the source/drain electrodes, the channel and the gate insulator layer. The top-contact structures, including the bottom-gate top-contact (BGTC) (inverted staggered) and the top-gate top-contact (TGTC) structure (co-planar), are used for manufacturing inorganic TFTs. For OTFTs, because of vulnerability of the OSC layer to solvent and high energy ions, it is challenging to use either the sputtering and photolithograph processes or the direct printing approaches to form the electrodes on top. Although thermal

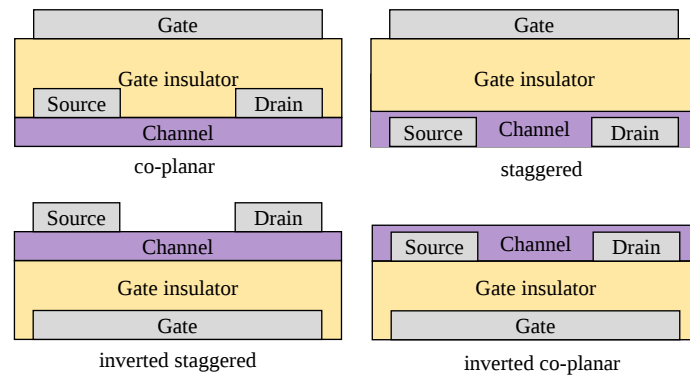


Fig. 1 Illustration of the four possible structures for fabricating TFTs, depending on the sequences of depositing various layers.

evaporation via shadow masks can be used to make patterned electrodes on top of the OSC layer, the achievable resolution and pattern complexity is quite limited for large area manufacturing. Therefore, the bottom-contact structures are more suitable for large area manufacturing of OTFT integrated circuits or high-resolution arrays. Compared to the bottom-gate bottom-contact (BGBC) structure, the top-gate bottom-contact (TGBC) one normally owns larger carrier injection area and thus smaller contact resistance, and in turn is more suitable for building high performance short channel devices (Han *et al.*, 2019; Feng *et al.*, 2018).

The dual-gate structure as shown in Fig. 2 is also investigated for OTFTs by adding the second gate on the other side of the OSC layer. Despite of more complexity in processes, the dual-gate structure brings several benefits for performance improvement. Firstly, presence of the two gates can shield the channel from the ambient light to improve the device stability. Secondly, by electrically connecting the two gates, stronger electro-static control of the channel can be achieved for larger ON-state current and smaller leakage current. Another merit of the dual-gate structure is its capability of threshold voltage modulation with help of the second gate, which is important for the OTFTs to meet various circuit design requirements (Feng *et al.*, 2018; Myny *et al.*, 2011).

For many circuit integration applications, the device dimension needs to be scaled down to improve the integration density, the current driving capability, and the operation frequency. As the channel length being scaled down and the mobility of the OSC layer being improved, the source/drain contact resistance and the overlap parasitic capacitance between the gate and the source/drain becomes the bottleneck for further performance improvement (Klauk 2018). To minimize the contact resistance, it is important to combine OSC material design and contact interface engineering for different device structures (Han *et al.*, 2019; Feng *et al.*, 2018).

Processes for Integration

To fabricate the multi-layer OTFT structures in solution processes, deposition of different layers sequentially could cause dissolution or swelling of the underlayer. The underlayer thus needs to be strongly resistant to the solvent used for depositing the subsequent layer. For the bottom-gate structure, the gate insulator layer is deposited before the OSC layer, and photo- or thermal crosslinking of the polymer dielectrics can be used to enhance solvent resistance and the electrical robustness (Wang *et al.*, 2013; Li *et al.*, 2015). For the top-gate structure, the OSC layer is deposited before the GI layer. Although it is also possible to crosslink the polymer OSCs, the electrical properties will be affected by the crosslink process, causing limited device performance (Kaelblein *et al.*, 2016). Therefore, a more practical approach is to choose polymer dielectric material of solvent orthogonality, such as the fluoropolymer dielectric CYTOP and Teflon. To protect the device from influence of ambient moisture, an encapsulation or protection layer is also needed after completion of the intrinsic device part. In all, it is vital to develop a full material stack alongside the OSC to have well layer-to-layer matching in terms of both processing and electrical or physical properties.

For further circuit integration, the most ideal approach is full additive printing for “manufacturing-on-demand” at a fraction of the cost and footprint. Lots of research is thus undergoing on addressing issues on all printing processes, for many very cost-sensitive applications with less requirements on the integration density and reliability. However, due to difficulties in technology scaling for fine structures and complicated multi-layer integration, it is unrealistic to use all additive printing processes for large-scale high-density integration, which is required for displays and imagers. Thus, it’s clear in the short term, OTFT based high density integration must be manufactured using more conventional processes in the industry to minimize barriers of ramping-up for mass-production and validation of the value that can be brought to applications. OTFT manufacture can use the processes currently employed in the display industry, including sputtering, photolithography, wet etching, dry etching, spin coating and slot die coating. Materials used for the OSC layer are perhaps the most sensitive and exposure to oxidizing chemicals such as nitric acid and aggressive organic solvents such as photoresist stripper should be avoided throughout the process. Sputtering and dry etching can also have impacts on the OTFT characteristics of certain materials. Some degree of protection is thus often required by dielectric, metal or other photoresist layers throughout the processes so that aggressive chemicals and processes can be used. For example as shown in Fig. 3, a four-mask OTFT process flow using the gate electrode as the hard mask and the sputtering-resistant gate insulator layer as the protection layer was developed for high-resolution display integration (Li *et al.*, 2019; Han *et al.*, 2022).

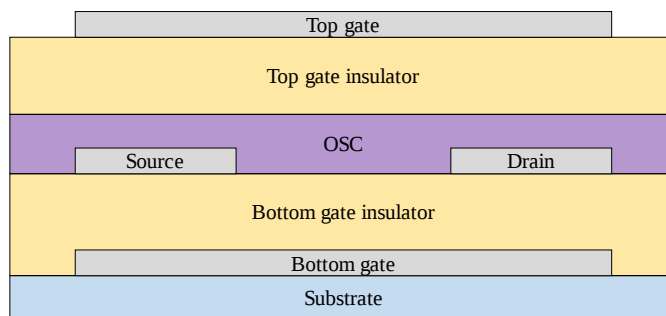


Fig. 2 Schematic of a dual gate OTFT structure.

With the high resolution patterning, good overlay accuracy and low defect density common to display manufacturing, it is proved that high performance with good uniformity can be achieved.

Competitive Advantages

Present the main contents of the article in logically arranged sections and subsections.

The inorganic TFT technologies as shown in [Table 1](#) in the display industry can nearly cover all needs of the main-stream displays, including LCDs, e-paper or AMOLED technologies for products ranging from mobile phones, e-readers to large size TV. After huge investment for the manufacturing facilities, the display makers are reluctant to adopt new material or processes for the TFT backplanes. For example, to develop flexible AMOLED displays, the industry preferred to improving high temperature tolerance of the plastic substrate instead of adopting new material TFT technologies of lower processing temperature. Therefore, the competitive advantages of OTFTs over the inorganic TFTs for display applications need to be re-considered.

Compared to those inorganic counterparts, OTFTs own several unique advantages for building ubiquitous displays, sensors and electronic systems, which require high customizability in performance, form factor and cost. Firstly, stacks of high quality organic OSC and polymer gate dielectric layers can be formed at very low temperature below 120 °C or even 100 °C, so that the common optically transparent or bio-compatible plastic films are able to be used as the substrates ([Fig. 4](#)). Matching of the OTFT stack layers with the plastic substrate in both thermal and mechanical properties significantly reduce the thermal stress during processing and the mechanical stress in use. Secondly, deposition of the organic layers with solution printing or coating processes can avoid complex and energy-intensive chemical reaction during manufacturing, which needs expensive infrastructure and maintenance cost. Thirdly, OSCs have great potential of further performance improvement and functionalization through molecule tailoring or physical blending, which might open a new way of technology transformation by changing the material instead of the equipment. The evolution of the OSCs would be able to provide a more economical way for technology upgradation rather than reinvesting the manufacturing facilities. Last but not the least, with versatile device structure and material choices available for making OTFTs, different functions can be easily integrated to create shatterproof flexible integrated systems in compact form factors with nearly no increase in thickness and weight. With these advantages, commercialization of the solution processed OTFT technology might adopt the “distributed” manufacturing model ([Fig. 5](#)) ([Guo et al., 2021](#)). It is more competitive to meet the requirements for diverse applications than the “centralized” manufacturing model with the inorganic technologies, by activating ubiquitous items with flexible displays, sensors and other electronic functions.

OTFTs for Displays

Discuss the potential developments and future directions in the area of the contribution here.

In the past, there have been lots of trials on making displays based on OTFT backplanes, including e-paper, AMOLEDs and flexible LCDs, as shown in [Fig. 6](#). For e-paper, the microcapsule electrophoretic display (EPD) is the most well commercialized technology. Although the driving scheme of EPDs is much more complex than that for LCDs, the pixel circuit is similar, consisting of one pixel switch TFT and one storage capacitor.

Key requirements of the TFT for pixel switches is low leakage current and large ON/OFF current ratio. In OSCs, the electron transport can be suppressed via molecule design to have p-type unipolar conduction. Therefore, even with a simple metal-semiconductor contact, very low leakage current ($< 10^{-17}$ A/ μ m) and large ON/OFF current ratio ($> 10^{10}$) can be achieved ([Fig. 7](#)) ([Han et al., 2022](#)). Therefore, the OTFT backplane is of great promise for active matrix EPDs, by providing equal or even better switching performance compared to the a-Si TFT, but at lower manufacturing cost and temperature. The low leakage characteristics are also promising for low fresh rate AMOLED displays to reduce power consumption.

To build transmissive flexible LCDs, transparent plastic substrate is required. However, polyimide (PI) is currently the only plastic substrate capable of withstanding the high temperature required for manufacturing inorganic TFTs. Although colorless PI

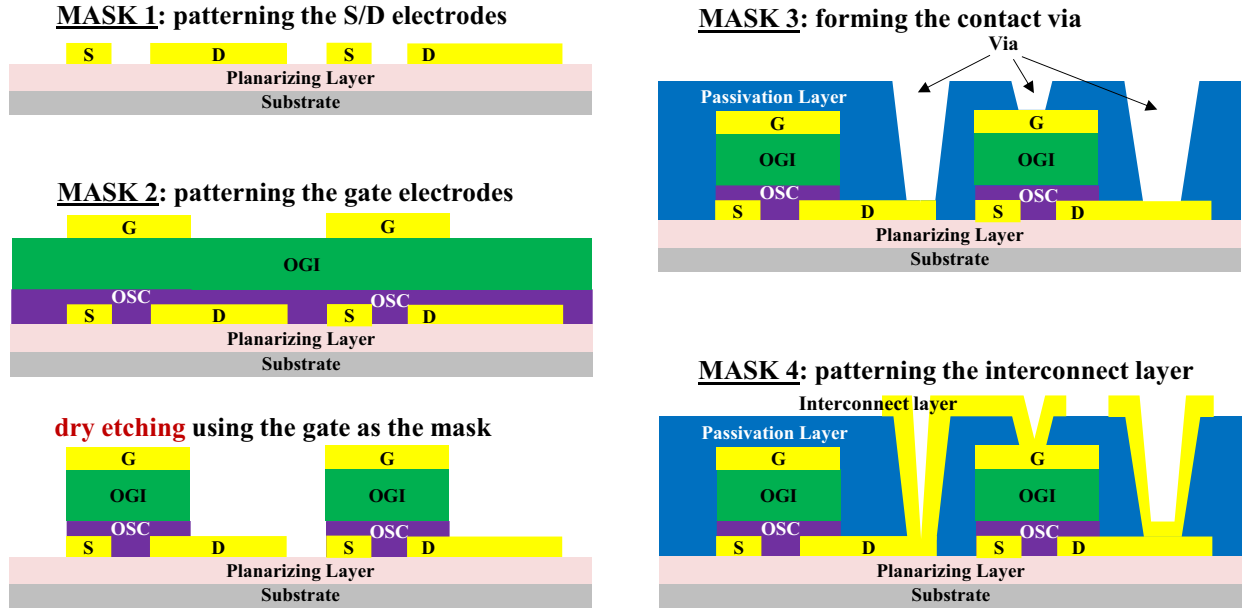


Fig. 3 Illustration a four-mask process flow for OTFT integration (Li *et al.*, 2019).

Table 1 Comparison of the existing TFT display backplane technologies

Technology	<i>a</i> -Si	LTPS	AOS
Mobility ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$)	0.5-1	~ 100	> 10
Lowest leakage ($\text{A} \cdot \mu\text{m}^{-1}$)	$\sim 10^{-15}$	$\sim 10^{-13}$	$< 10^{-18}$
Operational stability	—	+	—
Required processes	Sputtering PECVD Photolith Dry/wet etching	<i>a</i> -Si processes + ELA & Ion doping	Same with <i>a</i> -Si
Substrate size	Gen. 10	Gen. 6	Gen. 8
Max substrate Temp. ($^{\circ}\text{C}$)	< 350	~ 450	< 350

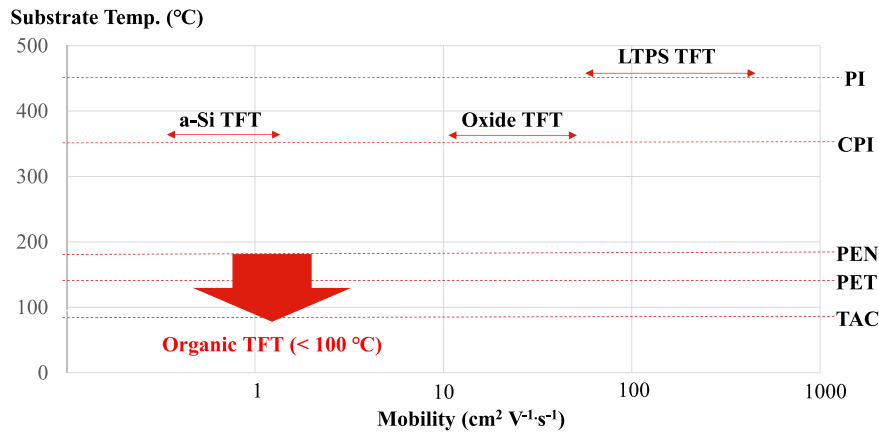


Fig. 4 Comparison of the OTFT with inorganic TFTs in maximum substrate temperature during processing and device mobility.

(CPI) substrates might be used, the optical properties of CPI substrates are inferior to the glass that they replace. The ability of the OTFT to process a complete active matrix backplane below 100°C opens up the opportunity to choose low cost optically transparent plastic film as the substrate, such as the triacetyl cellulose (TAC) film, which has already been used in displays for polarizers (Cain, 2018). The resulting whole material stack as shown in Fig. 8(a) appears quite familiar to that in the conventional LCD, but with TAC film in place of glass, and a complete OTFT materials set. The stack also makes use of many of the materials in the existing LCD supply chain (e.g. polarizers, backlight, LC material and others), and the cost structure is similar to a glass LCD.

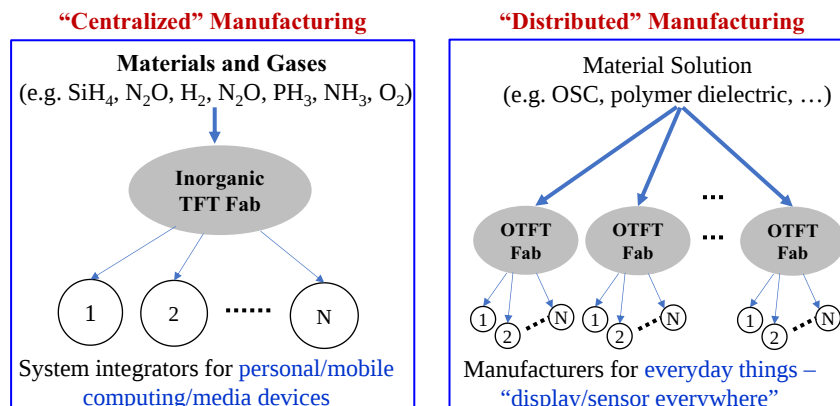


Fig. 5 Comparison of the “centralized” and “distributed” manufacturing modes for inorganic and organic TFTs.

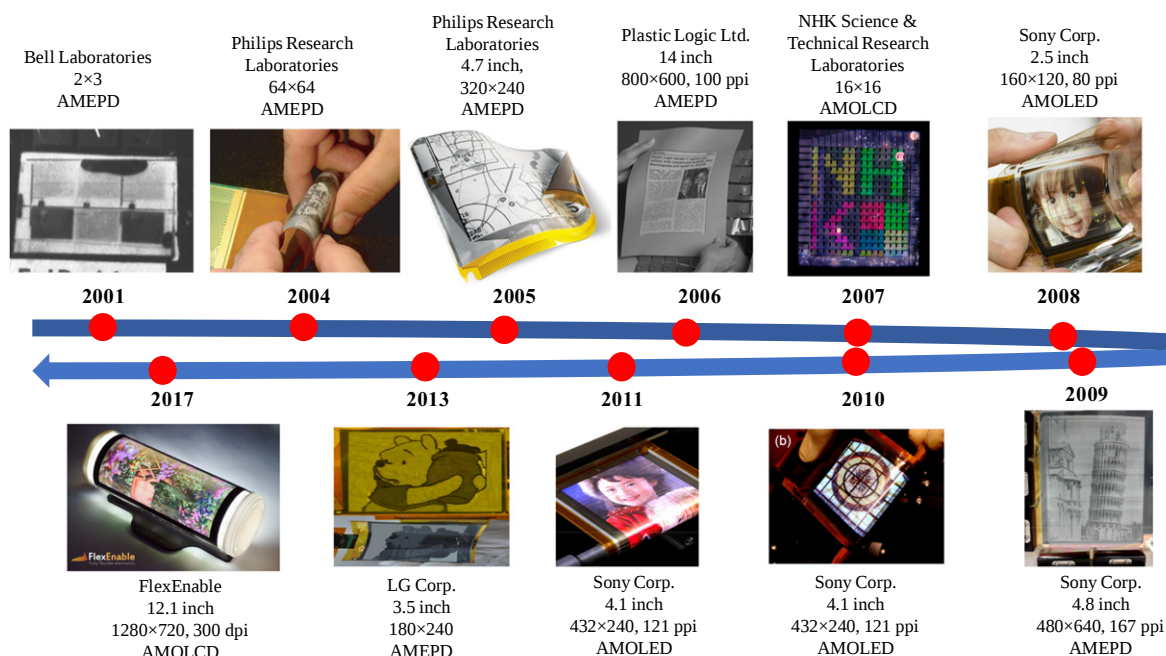


Fig. 6 The demonstrated OTFT based displays in previous SID conferences, including e-paper, AMOLEDs and flexible LCDs. (Guo *et al.*, 2021).

Whilst flexible OLED displays are already manufactured in volume, they are presently costly and as a result focused on flagship smart phone and smart watch applications. For flexible display applications, such as notebooks and tablets, smart home devices, automotive, monitors, TVs and digital signage, that require larger area or longer lifetime with high brightness, it is recognized that the attributes of flexible LCD technology might be well suited. For example, many smart speaker designs today are round or cylindrical, but glass displays are flat which limits their incorporation in non-rectangular form factors. By using flexible LCD, wrap-around screens are possible, and can provide a better user experience by enabling new audio-visual use cases without compromising the product design and aesthetics (Fig. 8(b)).

OTFT for Sensors

With flexibility in device architecture and integration of various sensing materials or structures, an OTFT, in principle, can be designed to transduce various kinds of sensor signals (e.g. bio-chemical, gas, pressure and electrophysiological signals) to channel current output changes as shown in Fig. 9. Though an OTFT-only “stand-alone” sensor system would be ideal for lower cost and shorter design-to-product time, it is extremely challenging to achieve the circuit complexity and performance equivalent to that of the silicon ICs due to larger feature size and poor carrier mobility. Therefore, a flexible hybrid integration (FHI) scheme as illustrated in Fig. 10 is more realistic for ubiquitous sensor systems by combining the advantages of both the silicon ICs and the

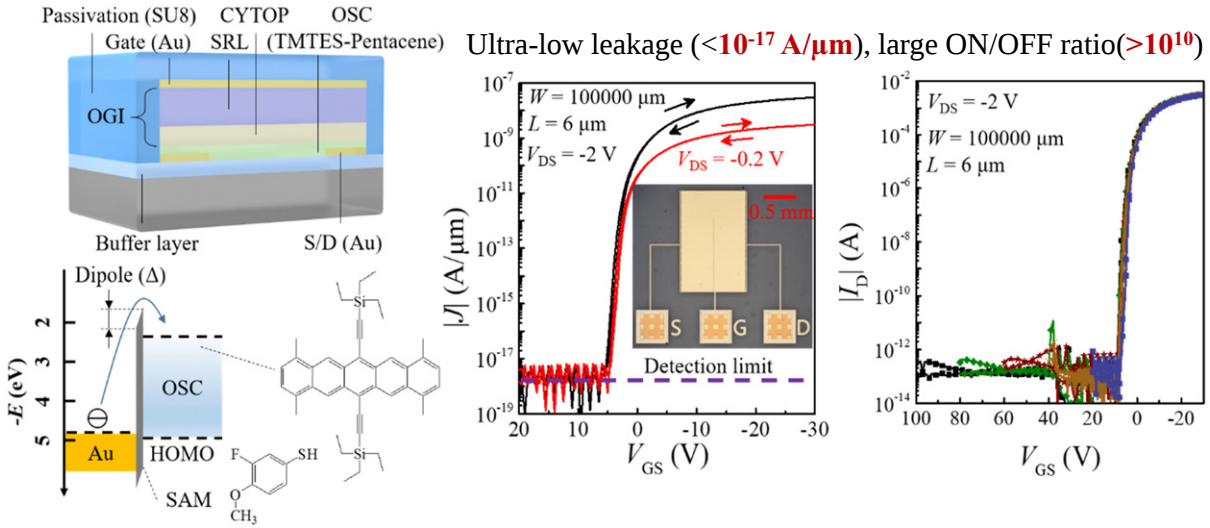


Fig. 7 Solution processed top-gate bottom-contact OTFT presenting ultra-low leakage current and large ON/OFF ratio (Han *et al.*, 2022).

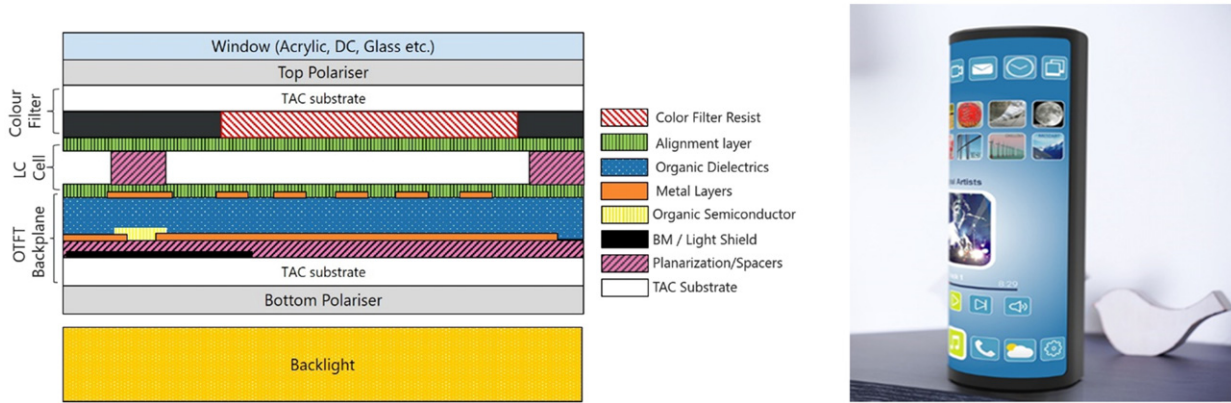


Fig. 8 Illustration of the whole material stack of the OTFT flexible LCD (Source: FlexEnable).

OTFT circuitry (Huang *et al.*, 2020). In such an architecture, the general-purpose ASIC performs sensor signal acquisition and conditioning, data processing and transmission, and power harvesting/management. The OTFT circuitry is able to realize flexible or conformable large area coverage with convenience of integrating different sensing materials or structures. The output current change of the OTFT induced by various sensed signals is then processed using the general-purpose ASIC with common analog interfaces. Moreover, the sensed signal is able to be amplified locally with a designed OTFT amplifier circuitry. With the OTFT switches, active-matrix sensor arrays can also be constructed to obtain spatial signal mapping. Integration of the ASIC and the sensor integrated OTFT circuitry could be realized by either packaging them onto a common plastic substrate, or bonding the ASIC die directly onto the OTFT circuitry substrate.

Most of application scenarios with such flexible sensor systems are very power-constrained. This poses a stringent requirement on the operation power of the OTFT circuitry. The operation power might be composed of the dynamic part and the standby part. The former is proportional to CV^2 , where C is the capacitance and V is the voltage swing. The latter is determined by the leakage current. Therefore, for low power operation, it is important to reduce the required operation voltage while maintaining low enough leakage current. The methods of using a thin or high- k gate insulator (GI) layer or a GI layer to enlarge the GI capacitance have been widely used to decrease the subthreshold swing of OTFTs for low operation voltage. However, thinning GI is not practical for large area solution processes. The GI layer needs at least a few hundred nanometers for good enough insulation to achieve low leakage current. Adopting high- k dielectric can help to realize low voltage OTFTs based on thick GI layers, but the localized dipole electric field could affect the carrier mobility and reliability (Veres *et al.*, 2003). It is also an issue to find suitable high- k polymer dielectric materials for low temperature solution processes.

To address the above issue, an approach to realize low voltage OTFTs by reducing the sub-gap trap-state density at the channel interface was developed (Feng *et al.*, 2013). With this approach, low voltage OTFTs can be fabricated at small GI capacitance, and exhibits excellent operational stability (Fig. 11) (Tang *et al.*, 2015; Guo *et al.*, 2021). This approach enables to fabricate low voltage OTFTs with low- k thick GI

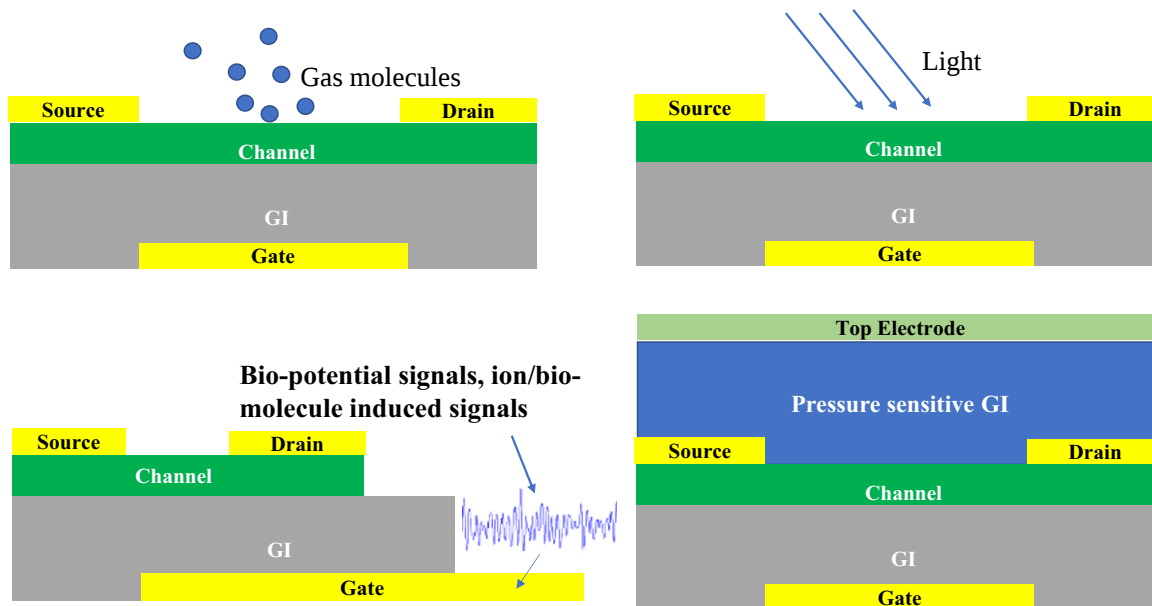


Fig. 9 Illustration of using an OTFT in bottom-gate bottom-contact structure to implement various sensing transducers.

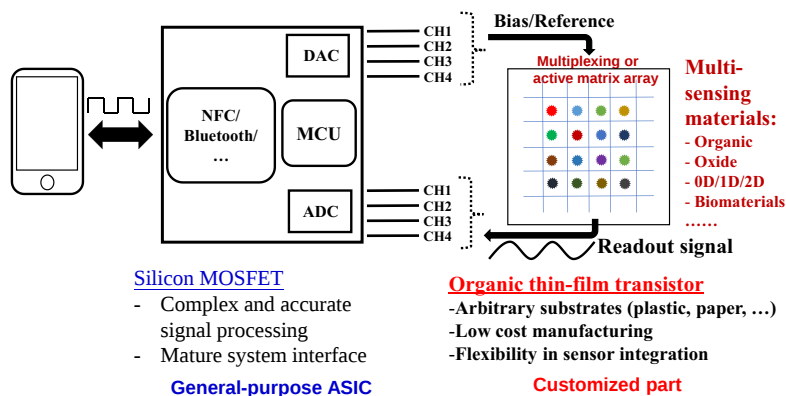


Fig. 10 Schematic of the flexible hybrid integration (FHI) architecture composed of the silicon MOSFET IC and the organic thin-film transistor (OTFT) circuitry.

layers, and has been implemented with various OSC and GI materials (Feng *et al.*, 2016; Zhao *et al.*, 2017a; Shiwaku *et al.*, 2017; Kuniit *et al.*, 2016; Jiang *et al.*, 2019). Being operated with a similar low voltage but at a GI capacitance much smaller than that of conventional low voltage OTFTs, the device owns higher power efficiency (Tang *et al.*, 2015). With OSC of p-type unipolar conduction and a thick GI layer, leakage through the channel and the GI layer can be suppressed, resulting in very low leakage current. The features of low operational voltage and low leakage make this device a promising technology to be used for the low power FHI sensor systems.

This low voltage OTFT technology has been applied to construct various transducers for gas, optical, pressure, bio-potential, ion and bio-molecule sensing (Feng *et al.*, 2016; Zhao *et al.*, 2017b; Tsuji *et al.*, 2017; Jiang *et al.*, 2019; Tang *et al.*, 2022). For biochemical sensing in liquid solution environment, integration of the sensing and reference electrodes (SE and RE) with the OTFT circuitry in a small device footprint is important to reduce the amount of required solution and also suppress external noise influence. On the other hand, a certain distance is needed between the SE/RE pair and the OTFT part to encapsulate the latter from the analyte solution, leading to large feature sizes. A through-plastic-via three-dimensional (TPV-3D) integration approach is developed to address the issue (Han *et al.*, 2021) (Fig. 12). Based on this approach, the SE is fabricated on a different plastic substrate without concern of affecting the OTFTs. A simple OTFT amplifier is integrated with the SE/RE pair for H⁺ detection, showing the weak ion response (~ 7 mV induced by 0.2 pH) can be amplified by 10 times. It is beneficial for improving signal-to-noise ratio and improving the detection limit.

Combining this OTFT bio-sensor technology and a 13.56 MHz RFID IC chip, FHI is achieved to make a RF powered mobile bio-sensing platform with friendly connectivity to the smartphone as shown in Fig. 13 (Ouyang *et al.*, 2021). Buffer solutions of

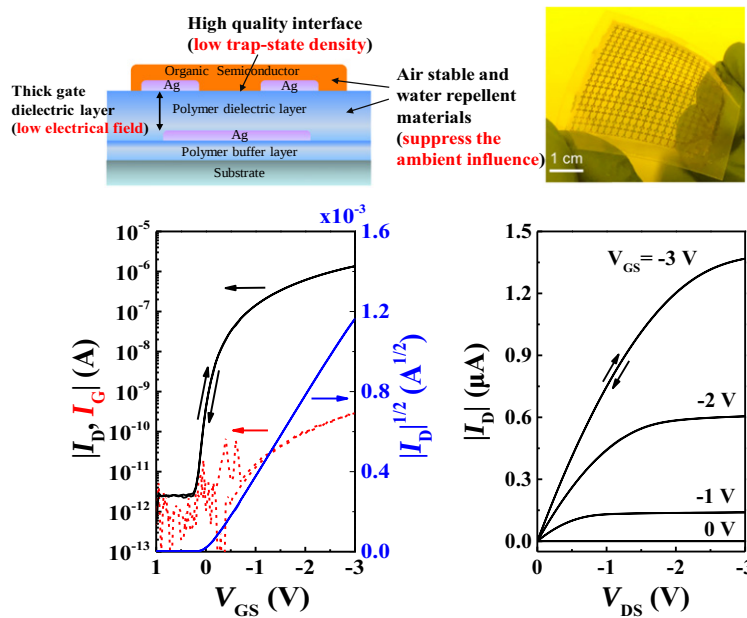


Fig. 11 Illustration of the bottom-gate bottom-contact structure low trap-state density OTFT with a blended solution of small organic semiconductor (TIPS-pentacene) and insulating polymer binder (PS) for low voltage operation, the photo image of the fabricated flexible OTFT devices and the measured typical current-voltage characteristics. (Guo *et al.*, 2021)

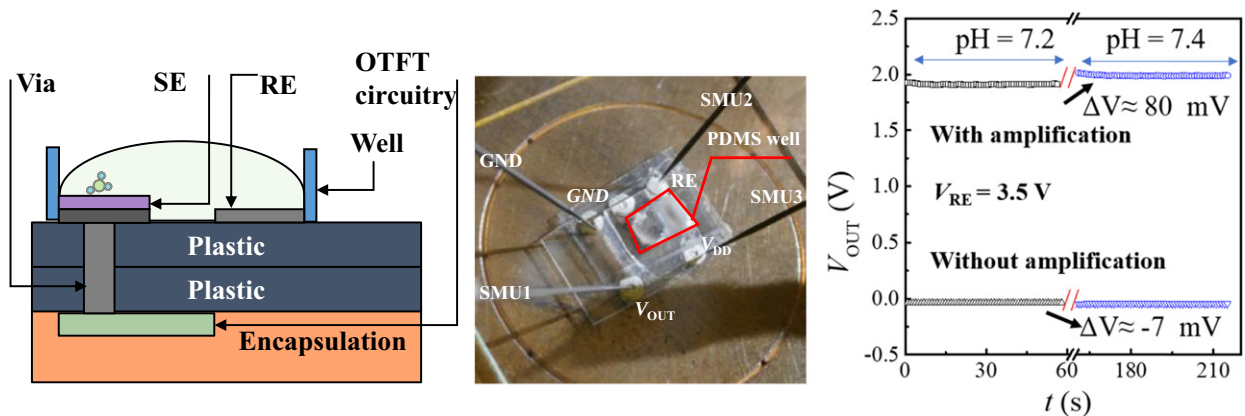


Fig. 12 Through-plastic-via three-dimensional (TPV-3D) Integration of an OTFT amplifier with the SE/RE pair for H^+ detection, showing that the weak response (~ 7 mV induced by 0.2 pH) can be amplified by 10 times. (Han *et al.*, 2021).

different pH values were dropped to the four points, and the readout results through the smartphone agree well with the pH value variations of the test buffer solutions

Future Directions

Despite of the advantageous features of OTFTs and also promising efforts on developing various displays and sensors based on OTFT, there are still several fundamental issues at the material and device levels to be addressed for developing a commercially competitive technology for mass-production and practical applications.

First of all, improving the performance of OSCs is still key. In the past, significant progresses have been made in the material and chemistry community on improving the OSC mobility. However, many molecule designs didn't consider scalable synthesis, processability and overall device performance (e.g. leakage, subthreshold swing and stability). Due to complex carrier modulation and transport mechanisms, material and device instabilities and presence of contact resistance, and so on, many of reported OTFTs present non-ideal field effect transistor (FET) behaviors. As a result, these high mobility values are shown to be significantly overestimated because the mobility extraction is based on the ideal FET model while neglecting the deviation of the

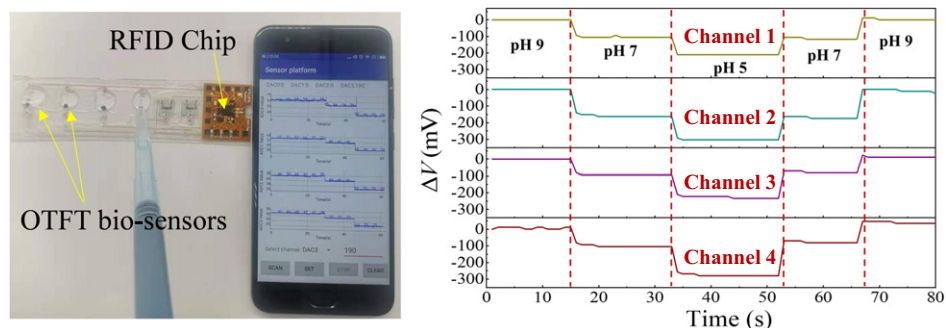


Fig. 13 Demonstration of a mobile ion-sensing platform by combining the OTFT bio-sensor technology and a 13.56 MHz RFID IC chip. (Ouyang *et al.*, 2021).

electrical behavior of the fabricated OTFTs from that of an ideal FET (Liu *et al.*, 2017; Choi *et al.*, 2017; Paterson *et al.*, 2018). Moreover, the claimed higher values have not yet been independently reproduced by at least one other research groups (Schweicher *et al.*, 2020). For these reasons, mobility of the OSCs suitable for multi-layer device and circuit integration towards functional applications is far lower than the above claimed values. High performance OSC material designs need to consider scalable batch synthesis, ease of large area processing and matching with other layers (i.e. gate dielectric, electrode and passivation layers) in a manufacturable way.

Secondly, for practical display and sensor applications, the devices might need to pass several harsh conditions and strict reliability tests with high humidity and high temperature. For example, for AMOLED display integration, it is still difficult for the completed OTFT backplane to sustain subsequent annealing processes with temperature higher than 200 °C before deposition of the OLED layers. To address it, the high temperature robustness of the OSCs needs to further improved, and a well-designed OTFT material stack is also important.

Thirdly, in OTFTs, the source/drain electrodes often use high work function metals including gold or silver, and require surface treatment to improve charge injection. However, for manufacturing, the source/drain electrodes have to be compatible with the industry available processes. Alternatives to gold and silver are thus vital, including indium tin oxide (ITO), molybdenum (Mo), titanium (Ti) and copper (Cu). For that, investigation of suitable surface treatment on these non-noble electrodes to form uniform OSC channel layer on top and low contact resistance is key.

Conclusions

Although the current inorganic TFT technologies in industry can well cover the needs of the main stream display products, there is still prospect for the solution processed OTFT technology attributed to its clear differentiation. For ubiquitous and diverse display and sensor applications, the demanded customizability in form factor, cost, and function will be very challenging for existing TFT technologies. Flexible EPDs and LCDs are expected to be the first entry in display applications for the OTFT. Combining the low voltage OTFT and the silicon IC, the FHI scheme owns core competitiveness in high customizability, low-cost manufacturing, ease of being scaled up, and convenience for sensor material integration with low operational power. These features make this OTFT based FHI technology a promising choice to develop ubiquitous sensor systems for a wide range of applications such as medical diagnostics, daily health care food/water quality inspection and chemical or biological process monitoring. To become a commercially competitive technology for mass-production, many fundamental issues still remain. It is important to develop a full package of materials alongside the OSCs to provide a total solution for large area manufacturing. Comprehensive understanding the interplay among device structure, material stack, processing, performance and reliability is also needed.

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Organic Solar Cells

Lluís F Marsal, Department of Electric Electronic and Automatic Engineering, Universitat Rovira i Virgili, Campus Sescelades, Tarragona, Spain

José G Sánchez, Institute of Chemical Research of Catalonia-The Barcelona Institute of Science and Technology (ICIQ-BIST), Tarragona, Spain

Alfonsina AA Torimuntun, Department of Electric Electronic and Automatic Engineering, Universitat Rovira i Virgili, Campus Sescelades, Tarragona, Spain

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Abstract

During the last 5 years, the efficiency of organic solar cells has rapidly increased and currently is near the 20% milestone. The key to such high efficiencies mainly lies in developing novel donor and acceptor materials. This article presents the basics of organic solar cells, addressing the electronic structure of organic semiconductor materials, and the working principles of organic solar cells, from the generation to the extraction of free charge. Further, several strategies to improve the performance and stability of OSCs e.g., device structures, design of novel organic semiconductors materials, and interface engineering are discussed.

Nomenclature

Ag Silver
AM 1.5G Air mass 1.5 Global
BDT Benzodithiophene
BHJ Bulk heterojunction
Ca Calcium
CdTe Cadmium telluride
CIGS Copper indium gallium selenide
CSP Concentrating solar power
CT-state Charge-transfer state
D/A Donor/Acceptor
DIO 1,8-diiodooctane
E_g Energy gap
ETL Electron transporting layer
FF Fill factor
FA Fullerene acceptor
HOMO Highest occupied molecular orbitals
HTL Hole transporting layer
ITO Indium tin oxide
iPSCs Inverted polymer solar cells
J Current density
J_{ph} Photo-current density
J_{sc} Short circuit current density
J-V Current density versus voltage
LUMO Lowest unoccupied molecular orbitals
Mw Molecular weight
NFA Non-fullerene acceptor
n_{id} Ideality factor
OSCs Organic solar cells
PCE Power conversion efficiency
PSCs Polymer solar cells
PV Photovoltaics
R_s Series resistance
R_{sh} Shunt resistance
T Temperature
TOSCs Ternary organic solar cells
V Voltage
V_{oc} Open circuit voltage
WF Work function

Key Points

- The main objective of this article is to understand the principles and operating of organic solar cells.
- The article aims to contribute to identifying the key parameters to improve both efficiency and long-term stability of organic solar cells.
- The article presents the development and evolution of organic solar cells overtime.
- The article provides the state of the art of the efficiency of organic solar cells, and the upcoming research challenges for further applications.

Introduction

The concern on the continuous growth of energy demand by the human population and industry, together with the global warming led by fossil fuel burning (i.e., coal, oil, and gas) encourages the growth of clean-energy generation. Clean energy is produced by the so-called natural renewable energy sources (they are called renewable due to the capability to be naturally replenished) such as wind, sun, water, heat, and biomass. Among them, solar power is one of the most attractive energy sources due to the enormous electromagnetic radiation constantly supplied by the sun (120,000 terawatts). Currently, two leading solar energy technologies employ solar radiation to generate electrical power indirectly or directly: concentrating solar power (CSP) and solar photovoltaics (PV). On one hand, CSP indirectly generates electrical power since requires using mirrors to concentrate the sunlight energy to power a heat engine of a turbine that generates the electricity. On the other hand, solar PV technology (named solar cells) directly converts sunlight energy into electricity through the photovoltaic effect. In 1839, A. E. Becquerel observed for the first time the photovoltaic effect in an electrolytic cell consisting of two connected platinum electrodes immersed in a silver bromide solution (Becquerel, 1839). W.G. Adams and R.E. Day observed for the first time the photovoltaic effect in a solid system made of selenium in 1877 (Adams and Day, 1877). Then, the first thin-film solar cell made from a layer of selenium covered with a thin film of gold was described by C. Fritts in 1883 (Fritts, 1883). It was only in 1954 when Chapin, Fuller and Pearson developed the first p-n junction silicon-based solar cell with an efficiency of 6% at Bell labs (Chapin *et al.*, 1954), which was the prototype of present photovoltaic cells. Thenceforth, the continuous research on monocrystalline or polycrystalline silicon-based solar cells (referred to as first-generation solar cells) has allowed reach efficiencies of over 26% (Green *et al.*, 2022). Asides from their high efficiency, the long-term stability stands silicon solar cells leading the photovoltaics market. Nevertheless, the high amount of high-purity silicon and the complex fabrication process increase manufacturing costs.

Second-generation solar cells (or thin-film PV) arose as a solution to the drawbacks of high material usage and manufacturing costs of silicon solar cells. The use of high light absorption inorganic components such as amorphous silicon (a-Si), cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) instead of crystalline silicon simultaneously reduces the material-consumption and manufacturing costs. Despite their good stability and efficiencies of over 24% (Nakamura *et al.*, 2019), some production issues such as the need for high-vacuum and high-temperature conditions, besides some environmental issues have limited the large-scale fabrication of thin-film PVs. To achieve low-manufacturing costs and high-efficient thin-film solar cells, several emerging PV technologies (referred to as third generations PVs) have been developed. Third generation includes copper zinc tin sulfide (CZTS, 12.62%) (Son *et al.*, 2019), dye-sensitized solar cells (DSSCs, 13.5%) (Zhang *et al.*, 2021), quantum dot solar cells (QDSC, 18.1% from UNIST) (NREL, 2022), organic solar cells (OSC, 19.2%) (Zhu *et al.*, 2022), and perovskite solar cells (PSC, 25.5%) (Min *et al.* 2021). Among them, OSCs are one of the most attractive technologies due to their ability to absorb a large amount of sunlight using nanoscale-thin films, lightweight, low environmental impact, low-cost solution-processing, and the ability to fabricate semi-transparent and flexible devices on a large scale.

Background/Fundamentals

Basic of Organic Solar Cells

The first report on electrically conducting organic polymers in 1977 (Shirakawa *et al.*, 1977) drove the research on different electronic devices based on organic materials, leading to reaching the first breakthrough in OSCs in 1986 with the report of the first solar cell fabricated from a bilayer of copper phthalocyanine and perylene derivatives, which reached an efficiency of 1% (Tang, 1986). Another important breakthrough came with the invention of the bulk hetero-junction OSCs (BHJ-OSCs) by blending a conjugated polymer and a fullerene in the active layer in 1995 (Yu *et al.*, 1995), which indeed is one of the keys to achieving high efficiencies. Following these milestones, several strategies have been developed to improve the efficiency and stability of OSCs to include this technology in the photovoltaics market. OSCs are typically fabricated with a stack structure in which an organic layer is sandwiched between an electron-selective layer and a hole-selective layer.

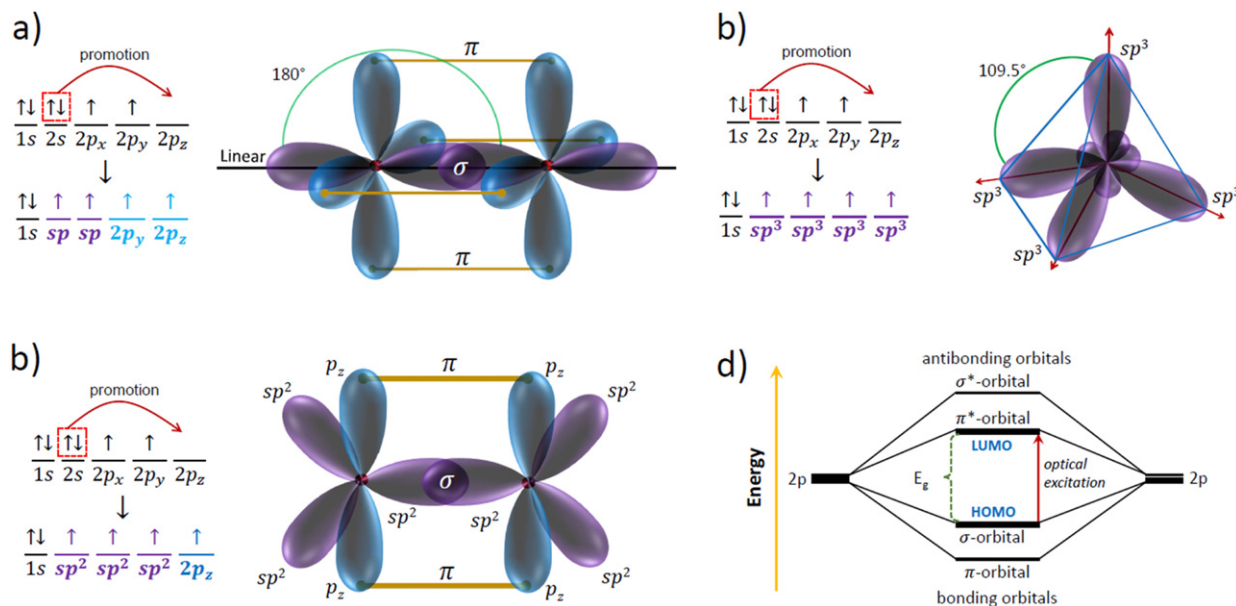
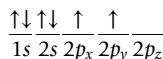


Fig. 1 Schematic representation of (a) sp^1 hybridization, (b) sp^3 hybridization, (c) sp^2 hybridization, and (d) Energy levels splitting of orbitals in a π -conjugated molecule.

Organic Semiconductor Materials

Organic semiconductors are materials mainly based on carbon and hydrogen atoms, and some hetero atoms such as oxygen, nitrogen and sulfur. The semiconducting properties of these materials lie in the alternation between single and double carbon-carbon bonds. The single bonds (so-called σ -bonds) are associated with localized electrons, and double bonds contain both σ and π -bonds. The electronic configuration of carbon in the ground state is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$. According to this, carbon atoms should form two covalent bonds due to their two unpaired electrons:



However, it is well known that carbon atoms can form four covalent bonds. To do so, one electron must be promoted from orbital $2s$ to the orbital $2p_z$, which leads to the generation of four sp hybrid orbitals. The orbital hybridization of carbon atoms allows them to bond to themselves (and to other atoms) with sp^1 , sp^2 , and sp^3 hybrid orbitals. In sp^1 hybridization, the $2s^2$ orbital and one of the $2p$ orbitals combine to form two sp orbitals (each composed of 50% s and 50% p), leaving the other $2p$ electrons unchanged. This results in a linear arrangement with an angle of 180° between bonds, which reduces electron repulsion. The two other $2p$ orbitals at 90° to one another, and the two sp orbitals are available for π -bonding. **Fig. 1(a)** shows the sp^1 hybridization of carbon. In the case of sp^3 hybridization, the $2s^2$ and the three $2p$ orbitals are combined, and four hybrid sp^3 bonds (σ -bonds) are formed with a bond angle of 109.5° . Therefore, the materials with this type of hybridization are poor conductors because all electrons are well localized in the σ -bonds (Brütting, 2006; Salaneck *et al.*, 1999). **Fig. 1(b)** shows the sp^3 hybridization of the carbon.

The sp^2 hybridization

In organic semiconductors, carbon atoms are sp^2 hybridized, where the hybridization of the $2s$ and $2p$ orbitals forms three sp^2 orbitals and leaves the $2p_z$ orbital unchanged. The sp^2 orbitals are positioned at 120° between them forming a triangle in a plane, while the p_z orbital is placed in the plane perpendicularly to the three sp^2 orbitals (Salaneck *et al.*, 1999). The overlap of sp^2 orbitals results in stronger σ -bonds, while the overlap of p_z orbitals forms delocalized π -bonds (see **Fig. 1(c)**). π -electrons have higher mobility than the σ -electrons because they can freely move between carbon atoms (Kyminsis, 2009). The delocalized π -electron is responsible for the semiconducting properties in organic materials. On the other hand, the ability of organic materials to absorb photons lies in the antibonding π^* -state, which is energy near to that of the π -state. The interactions of π^* -antibonding orbitals form a conduction band, so-called lowest unoccupied molecular orbitals (LUMO), whereas the interactions of π -orbitals yield a valence band known as highest occupied molecular orbitals (HOMO). The energy difference between HOMO and LUMO is well known as the energy gap (E_g), which is ranged around 1.1–3.5 eV for photoactive materials (Wu *et al.*, 2022). **Fig. 1(d)** shows the energy levels splitting of orbitals in a π -conjugated. The HOMO and LUMO determine the semiconducting and optical properties of organic semiconductors. The position of the absorption band of organic semiconductors is determined by the E_g of HOMO-LUMO. Moreover, the LUMO determines the ionization potential and the HOMO, the electron affinity of the materials. These two properties define the ability to donate or accept electrons (Zhan *et al.*, 2003).

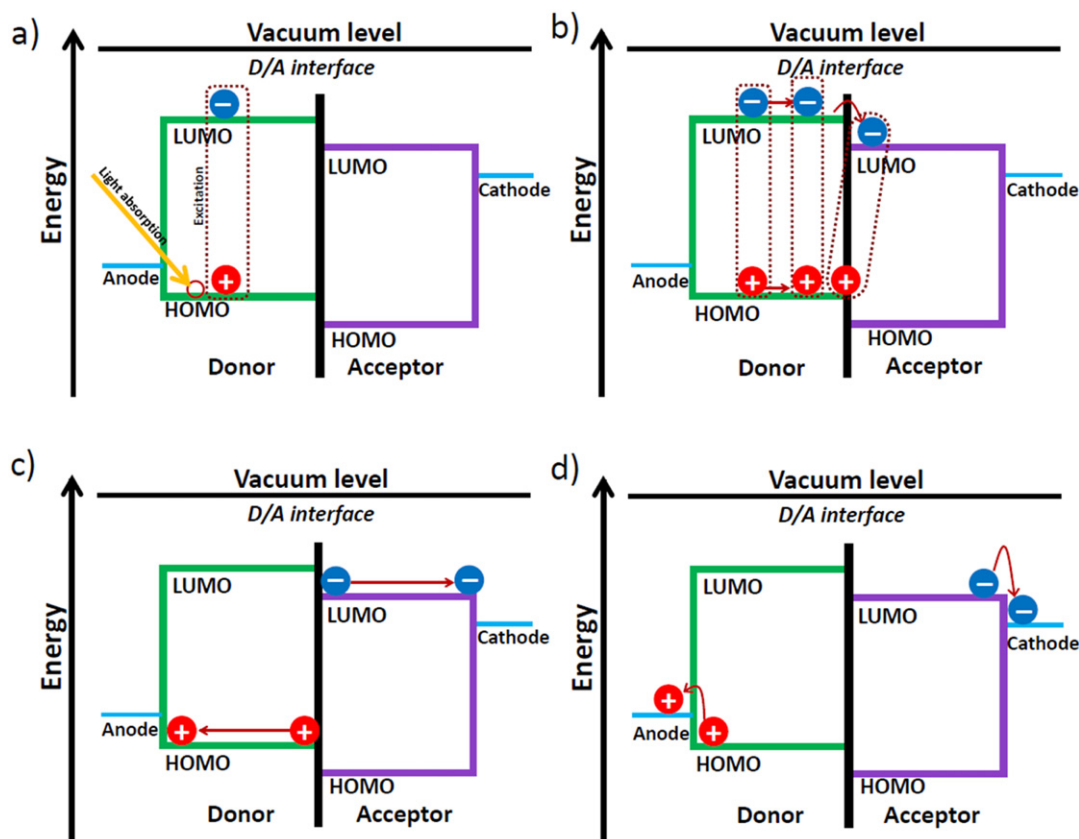


Fig. 2 Charge generation process in OSCs: (a) exciton generation, (b) exciton dissociation, (c) charge transporting, and (d) charge collection.

Organic semiconductors with higher HOMO levels usually work as electron-donor materials with a hole-transporting ability (*p*-type semiconductors), while those with lower LUMO levels can act as electron-acceptor and electron-transporting materials (*n*-type semiconductors). π -conjugated materials are molecules bonded by van der Waals forces, resulting in weaker intermolecular bonds. Consequently, the delocalization of electronic wave functions is much weaker, having a direct impact on the charge transport of the materials, which relies on hopping charges between localized states. The hopping rate in organic π -conjugated materials is usually described by two theoretical models: Miller-Abraham's formalisms and the Marcus theory (Marcus, 1993; Miller and Abrahams, 1960). Although Miller-Abraham's formalisms were used to describe the hopping rates in inorganic semiconductors, they are also often used to describe these in organic semiconductors because of their simplicity. On the other hand, Marcus' expressions calculate the hopping rate, considering an intermediate energetic barrier originated from energetic relaxation. Since efficient charge transport lies in the capability of charges to move from molecule to molecule, charge carrier mobility plays an important role in hopping transport. In organic semiconductors, the charge carrier mobility is influenced by several factors such as high electron-vibration coupling, weak electronic coupling, molecular packing, disorder, impurities, and molecular weight (Colladet *et al.*, 2007).

Physics of Organic Solar Cells

In a solar cell, the light absorbed by the semiconductor material results in the generation of excitons (electron-hole pairs attracted to each other by the electrostatic Coulomb force). The separation of excitons in free charges is caused by an electric field. This electric field is produced at the electrode junction to another material with a different work function (ionization energy) (Hill *et al.*, 2000). These processes are quite complex in organic semiconductors because of their chemical impurities, semi-crystalline lattice, and structural disorders. As a result, generated excitons diffuse as uncharged particles through the semiconductor until be dissociated by an electric field. The charge generation process in OSCs can be described in four steps as shown in Fig. 2: exciton generation, exciton dissociation, charge transport, and charge collection.

Exciton generation and dissociation

First, the incident photons are absorbed by the donor or the acceptor within the active layer. Then, the energy of the photon is transferred to an electron, resulting in the electron excitation from HOMO to LUMO (π - π^* transition). The photons absorption is limited by several factors such as the optical absorption coefficient, the bandgap (photons with energy $> E_g$ are absorbed), optical

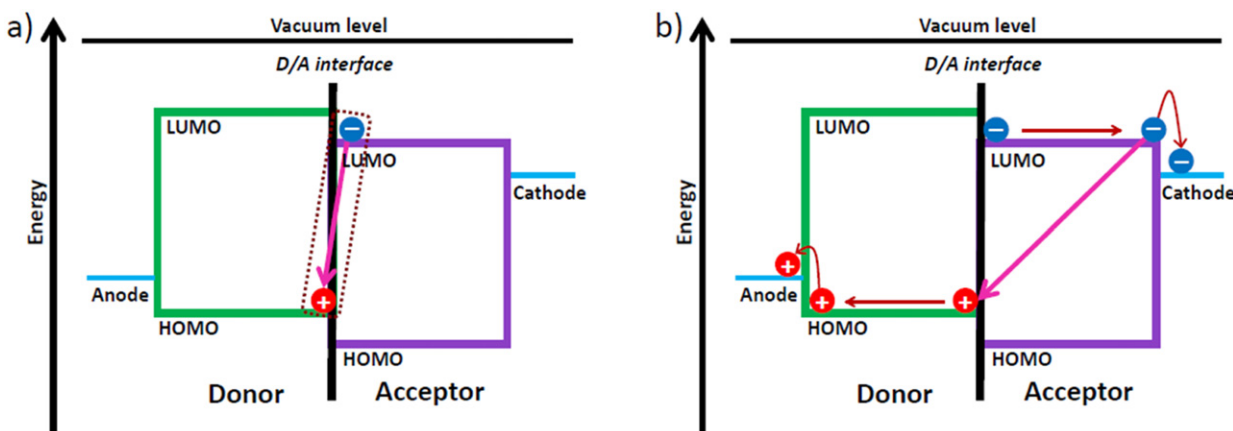


Fig. 3 (a) Geminate and (b) non-geminate recombination mechanisms.

losses (e.g., reflection, refraction and scattering), and the overlapping of the absorption spectrum of material with the solar radiation spectrum. Some organic semiconductors can absorb up to 77% of solar radiation on earth (Air Mass 1.5, or AM1.5) with thicknesses around 100–300 nm because of their relatively high absorption coefficients ($\sim 10^5 \text{ cm}^{-1}$). These materials have a wide optical absorption in the visible range due to their narrow absorption bands. As described in Fig. 2(a), after the absorption of the photon, the electrons are promoted from the ground state to the excited one, which generates an exciton (electron-hole pair bounded by electrostatic Coulomb force) (Cheng *et al.*, 2009; Schweitzer and Bässler, 2000). Subsequently, the generated exciton diffuses into the donor material until it reaches the donor/acceptor (D/A) interface, which is energetically favorable to dissociating exciton into free charge carriers. However, the distance that exciton can travel until reaches the D/A interface (called the exciton diffusion length, L_D) is short in the materials typically used in OSCs, which can limit the charge generation, i.e., between 5 and 20 nm for amorphous π -conjugated polymers and fullerenes, and 20–47 nm for non-fullerene acceptors (Firdaus *et al.*, 2020; Lin *et al.*, 2014; Sajjad *et al.*, 2020). The energy difference between the LUMO of the donor and acceptor (ΔLUMO) provides the energy necessary to dissociate the exciton into a free electron and an associated free hole (Sun, 2005). The energy needed for the exciton split into free charge is called exciton binding energy (E_b), and typically is in the range of 0.1–1.0 eV for organic materials (Knupfer, 2003; Li *et al.*, 2016). The free hole remains in the donor while the free electron is transferred to the acceptor, which takes an ultra-short time within 100 fs (Brédas *et al.*, 2009). Fig. 2(b) shows the exciton diffusion and separation into free charge carriers.

Charge transporting and collection

Upon exciton dissociation, the free charge carriers drift toward their corresponding electrode via the donor and acceptor materials. The electrons drift to the cathode through the acceptor, while the holes drift to the anode electrode through the donor as depicted in Fig. 2(c). In amorphous organic semiconductors, the charge transport mechanism is mainly performed by hopping transport. This mechanism is less efficient than others (e.g., band transport) since amorphous organic semiconductors exhibit high trap concentrations that result in low charge carrier mobility and charge recombination (Silinsh and Čápek, 1994). Finally, the free charges are collected at the electrodes. The electrons are collected at the cathode electrode and holes at the anode electrode as shown in Fig. 2(d). To perform an accurate charge carrier extraction, the LUMO level energy of the acceptor should be higher than that of the work-function of the cathode, while the HOMO level energy of the donor should be lower than that of the work-function of the anode. The difference between those energies offset determines the ohmic or Schottky contacts at the organic layer/electrode interface. The ohmic organic/electrode contact is the most preferable for a highly efficient charge collection. On the contrary, Schottky contact might cause electrical losses and lower charge extraction, resulting in a blocking contact. The charge collection efficiency is affected by several factors such as charge transfer, dipole formation, chemical reactions, traps within the organic material, and charge recombination (Colladet *et al.*, 2007).

Charge extraction limiting mechanisms

Several charge loss mechanisms (e.g., geminate, and non-geminate recombination) can take place during all processes from photon absorption to the collection of free charge carriers. The geminate recombination (also referred to as bimolecular recombination) describes the recombination of charge carriers during exciton dissociation, where the generated bound charges, or charge-transfer (CT) state, turn back to the ground state before dissociating into free charge carriers (Clarke and Durrant, 2010). Thus, the geminate recombination occurs after the exciton reaches the D/A interface and the electron-hole pair is separated, where the hole remains in the donor and the electron is transferred to the acceptor. However, the geminate electron-hole pair strongly remained bound at the interface due to the electron-hole Coulombic attraction. The geminate electron-hole pair must be dissociated into free charge carriers to avoid geminate recombination takes place (Proctor *et al.*, 2013). On the other hand, non-geminate recombination (also referred to as bimolecular recombination) describes the recombination of free electrons and holes after exciton is successfully dissociated into free carriers. The difference between geminate and non-geminate recombination

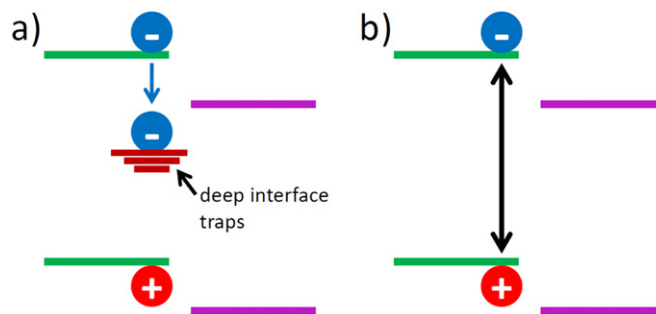


Fig. 4 Non-geminate recombination mechanisms: (a) Shockley-Read-Hall (or trap-assisted) recombination, (b) bimolecular Langevin recombination.

mechanisms lies in that the free electrons and holes do not originate from the same photon. The geminated and non-geminated recombination processes in BHJ organic solar cells are schematically represented in Fig. 3.

The non-geminate recombination is the primary loss process that limits the photocurrent generation in OSCs since it reduces the carrier lifetime and carrier density (Deibel *et al.*, 2010; Moses *et al.*, 1998). Non-geminate recombination occurs as three distinct mechanisms: trap-assisted (Shockley-Read-Hall/SRH), bimolecular (Langevin), and Auger recombination. In SRH recombination, a free charge carrier recombines with a deeply trapped opposite charge carrier.

Bimolecular recombination (described by the Langevin mechanism) takes place when low mobility free charge approaches the radius of the capture of another opposite free charge. Auger recombination is not observed in OSCs under 1 sun illumination since a higher charge density is required. In Auger recombination, the excess energy generated from the recombination of free charge carriers is given to a different free charge carrier, which is excited to higher energy states (Clarke and Durrant, 2010; Fukuhara *et al.*, 2020; Göhler *et al.*, 2018). Fig. 4 depicts the SRH (a) and Langevin (b) recombination mechanisms.

Main Body

Architecture of Organic Solar Cells

The main architecture of organic solar cells is consisting of an organic semiconductor active layer placed between two metals, which work as the anode and cathode electrodes. One of these electrodes (the front contact) must be highly semi-transparent to ensure maximum light absorption. A highly reflective metal is usually used as the back contact to redirect the non-absorbed light into the organic materials. The OSCs architecture plays an important role in the exciton dissociation and transportation of charge carriers. As aforementioned, the efficient exciton dissociation is mainly driven by the strong drop of potential at the interface donor/acceptor. Moreover, the difference between the effective work function of electrodes sets up a built-in potential (V_{bi}), which assists in photocarrier generation (Solak *et al.*, 2016). The most basic architectures of OSCs are single-layer, bilayer heterojunction, and bulk heterojunction. These architectures are based on active layers comprised of two materials (donor and electron acceptor), excluding the single-layer architecture which is comprised of only one material (Heremans *et al.*, 2009; Hoppe and Sariciftci, 2004). The main differences among the architectures of OSCs are the exciton dissociation and the charge transport mechanisms.

Single-layer OSCs

The single layer is the simplest architecture of OSCs, in which a photoactive organic material (typically p-type) is sandwiched between two electrodes with different work functions (Fig. 5(a)). A Schottky barrier is formed between the p-type organic semiconductor and the electrode with a lower work function (Sze and Ng, 2006). On the other hand, an ohmic contact is formed between the organic semiconductor and the electrode with a higher work function. The work function difference between the electrodes creates an electric field in the organic layer. The electric field causes the band bending of the HOMO and LUMO, starting at the Schottky barrier depletion region W (rich in electrons), close to the low work function electrode. Therefore, the electric field dissociates the excitons generated in the depletion layer and the free electrons are collected at the low work function electrode (Hoppe and Sariciftci, 2004). The free holes are transported through the organic semiconductor to the electrode with a high work function, as shown in Fig. 5(a). The single-layer OSCs exhibit low power conversion efficiencies ($< 1\%$). Since the exciton diffusion length is lower than 20 nm in organic materials, only the excitons generated in the depletion region contribute to the photocurrent. Moreover, the electric field is usually not strong enough to achieve an effective exciton dissociation. Since the free charge carriers move through the same material, the recombination depends on electron and hole concentrations (Halls *et al.*, 1996).

Bilayer heterojunction OSCs

The bilayer heterojunction architecture includes a donor and an acceptor material stacked together with a planar interface. The organic bilayer is placed between two electrodes with different work functions. In the bilayer OSCs, the exciton dissociation takes place at the planar interface by the effect of the large potential drop between donor and acceptor. To ensure an accurate charge

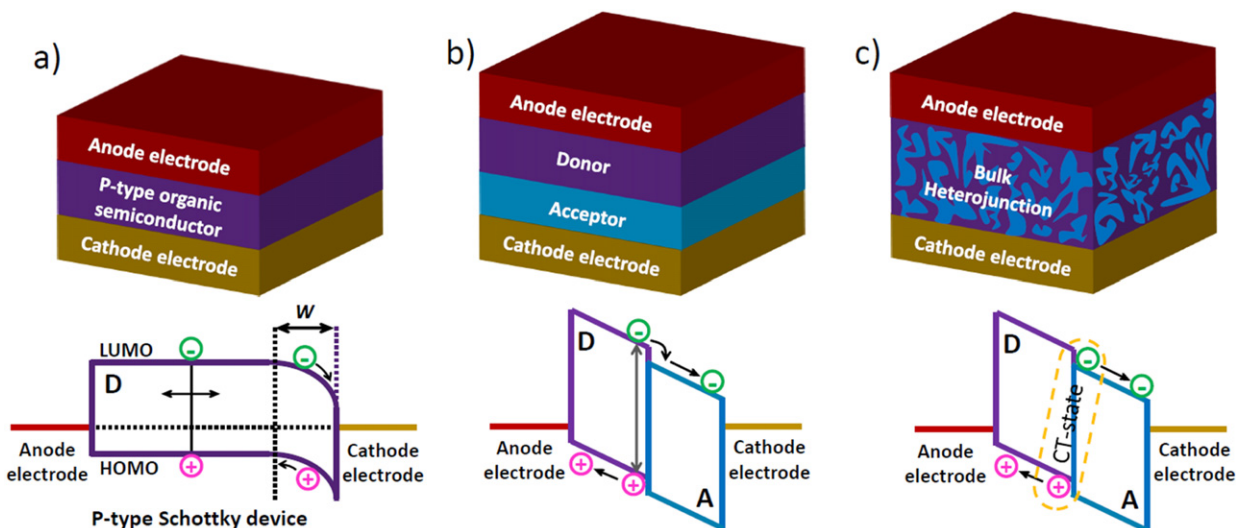


Fig. 5 (a) The device architecture of (a) single-layer semiconductor in single-junction, (b) bilayer heterojunction, and (c) bulk heterojunction with a conventional structure along with each energy alignment, and exciton diffusion and dissociation process.

extraction, the donor HOMO is matched to the electrode with a higher work function, while the acceptor LUMO is matched to the electrode with a lower work function (Tang, 1986). Fig. 5(b) shows the bilayer heterojunction architecture. Upon light absorption, the photogenerated excitons diffuse to reach the donor/acceptor interface, where the electron and hole are separated by the difference between the ionization potential and electron affinity of materials. Then, the holes remain in the donor HOMO and the electrons are transferred to the acceptor LUMO. The free charge carrier moves to their respective electrodes, the electrons at the low work function electrode and the holes at the high work function electrode, to be finally collected (Fig. 5(b)). The main advantages of this cell structure are the more efficient exciton dissociation and the monomolecular charge transport, thus the recombination is reduced, depending mostly on trap densities. Nevertheless, the efficiency of bilayer OSCs is still low, since the exciton diffusion length is only of few nanometers and the typical donor layer needs a thickness of at least 100 nm to absorb enough light (Kim *et al.*, 2014). A thicker layer can provide enough light absorption; however, the exciton can be generated far from the donor/acceptor interface increasing the probability of recombination.

Bulk heterojunction OSCs

In bulk heterojunction OSCs, the donor and acceptor materials are mixed to form a blend that will be used as the active layer. Thereby, the donor/acceptor interfacial area within a distance less than the exciton diffusion length is maximized. The operation principle of bulk heterojunction OSCs is like the bilayer one, but the donor/acceptor interface area for exciton dissociation is largely increased (in comparison to the planar bilayer architecture) allowing the efficient exciton dissociation everywhere in the bulk. The increment of the donor/acceptor area lies in the formation of the interpenetrated network due to phase segregations (Yu *et al.*, 1995). The architecture of bulk heterojunction OSCs is depicted in Fig. 5(c). Bulk heterojunction OSCs exhibit much higher efficiencies (in comparison to bilayer OSCs) since the interpenetrated network dispersed in the bulk improves the dissociation of the excitons. Unlike bilayer OSCs, in which the donor/acceptor materials contact their corresponding electrode, in bulk heterojunction OSCs the donor and acceptor phases form a bi-continuous and interpenetrating network determining the shape, crystallinity and orientation of the active layer (Dang *et al.*, 2013). Nevertheless, the transport of free charge carriers through the donor or acceptor phases to the electrodes is limited by the non-continuity in the interpenetrating network. The non-continuity in the interpenetrating network and the typically low charge carrier mobility of organic semiconductors increase the probability of non-geminate recombination of generated free charge carriers. Thus, the bulk heterojunction OSCs are sensitive to the nanoscale morphology of the blend, which depends on the conditions of the manufacturing process such as donor:acceptor ratio, solvent, solvent additive, thermal annealing and post-annealing, and solvent annealing, among others (Dyakonov, 2002; Schilinsky *et al.*, 2002).

Interfacial buffer layers

The heterojunction between the organic semiconductors and the electrodes plays an important role in device performance since charge extraction takes place at these interfaces. A low-quality organic/electrode interface can limit the charge extraction by appearing resistance effects, which decrease the power conversion efficiency of the device. For this reason, the HOMO and LUMO levels of organic semiconductors should be considered during the electrode choice. The most common material used as a front anode electrode is indium tin oxide (ITO) because of its high transparency, semiconducting properties, and the ability to form an ohmic contact with the HOMO level of donor material (Po *et al.*, 2011; Yip and Jen, 2012). Some low-work function metals such as calcium (Ca), magnesium (Mg), and barium (Ba) are commonly used as back cathode electrodes due to their capability to form an ohmic contact with the LUMO of organic materials. However, the high reactivity of these materials with water and oxygen reduces the

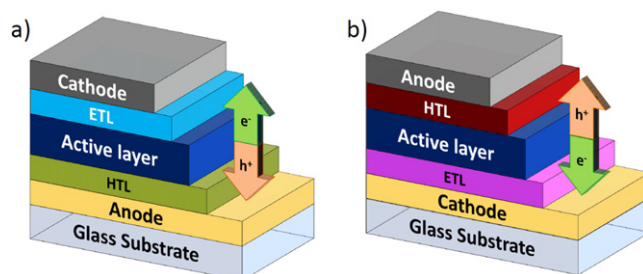


Fig. 6 Organic solar cell with (a) conventional and (b) inverted architecture.

lifetime of devices. Several high-work function metals such as gold (Au), silver (Ag) and aluminum (Al) have been used to replace Ca, Mg or Ba as the cathode. Despite these metals increasing the stability of OSCs, the higher mismatch between their work function and the HOMO level of organic materials generates a barrier layer that decreases the electron collection. After great efforts to overcome these problems, it was discovered that a thin layer between the electrodes and the organic semiconductors can improve charge collection and extraction. These layers are called buffer layers, interfacial layers, or interlayers. The effectivity of these layers is based on their ability to improve the energy-level alignment between HOMO and LUMO levels of organic materials with the work function of electrodes (Lai *et al.*, 2013). Materials such as metals, neutral polymers, salts, metal oxides, and polyelectrolytes are usually used as buffer layers in OSCs. The buffer layer between the cathode and the acceptor improves the electron transporting and collection, known as the electron transporting layer (ETL). On the other hand, the buffer layer between the anode and the donor, known as the hole transporting layer (HTL), improves the hole transporting and collection (Yin *et al.*, 2016).

OSCs with inverted architecture

The conventional architecture of OSCs used Ca and PEDOT:PSS/indium tin oxide (ITO) as low and high work-function metal cathode and anode, respectively. However, it is well known that calcium can easily be oxidized in the presence of oxygen. In addition, the hygroscopic and acidic nature of PEDOT:PSS may degrade the ITO electrode and active layer, which results in a stability reduction of solar cells. All these aspects degrade the interfaces, so the resulting devices are not very stable (Jørgensen *et al.*, 2008). Unlike conventional architecture that is illuminated through a transparent anode, the inverted OSCs (iOSCs) reverse the buffer layer sequence to improve device stability and performance. As a result, the transparent anode becomes the transparent cathode, and the charge carriers are transported in the opposite direction. Thus, the charge is collected in the opposite electrodes, i.e., in conventional OSCs, the holes are collected in the transparent electrode and the electrons in the top metal electrode, whereas, in iOSCs, the electrons are collected by the transparent electrode and the holes by the top metal electrode (Fig. 6). The inverted device design became an effective strategy to improve the performance and stability of OSCs. The long-term stability under ambient conditions arises from the self-encapsulating by the use of air-stable hole transporting materials for the top contact instead of PEDOT:PSS. In addition, the high work function (> 5 eV) of some air-stable transition metal oxide, e.g., MoO_3 , V_2O_5 or NiO , provide low resistance ohmic contacts at anode electrode (Greiner *et al.*, 2012), whereas the Ca is largely replaced by ZnO or TiOx as the ETL.

Performance Parameters of Organic Solar Cells

The most common method to characterize the photovoltaic performance of OSCs, as well as their electrical properties, is the measurement of their current density-voltage characteristics (J - V curve) in the dark and under illumination conditions. For an accurate characterization, the J - V measurement should be performed under standard Air Mass 1.5 Global (AM 1.5 G) illumination conditions at a device temperature of 25°C . The term "Air Mass 1.5" denotes 1.5-atmosphere thickness, corresponding to 48.2° solar zenith angle while the term "Global" refers to both direct and diffuse radiation (Gueymard *et al.*, 2002). The primary performance parameters of OSCs such as open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF) and power conversion efficiency (PCE) can be obtained from the J - V characteristic under standard illumination conditions. Among these, the PCE is the most important parameter since it describes the ratio between the incident light and the maximum output power. The typical J - V characteristics and the photovoltaics parameters of OSCs measured in the dark and under standard illumination conditions are depicted in Fig. 7. The OSCs measured in dark conditions exhibit a similar current density-voltage behavior to that of an ideal p-n junction diode. The current density can be described as follow (Nelson, 2003):

$$J_{\text{dark}} = J_0 \left[\exp\left(\frac{qV}{n_{\text{id}}kT}\right) - 1 \right] \quad (1)$$

where J_0 is the saturation current density, q is the electronic charge, V is the voltage, n_{id} is the ideal factor of the diode, k is Boltzmann's constant, and T is the temperature. When the OSCs are measured under standard illumination conditions, a photocurrent J_{ph} is generated, thus resulting in a downward shift of the J - V curve as shown in Fig. 7 and Eq. 2.

$$J = J_0 \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] - J_{\text{ph}} \quad (2)$$

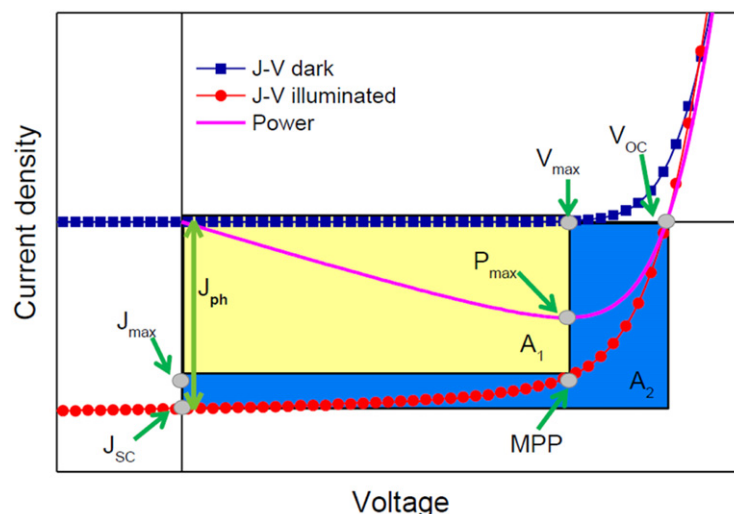


Fig. 7 Typical J - V characteristic and the photovoltaics parameters of OSCs in the dark and under standard illumination at 1 Sun (100 mW cm^{-2}).

Open circuit voltage (V_{OC})

The V_{OC} of OSCs under standard illumination conditions is the maximum voltage at which the net current in the device is zero. The V_{OC} is proportional to the difference between the LUMO energy level of the acceptor and the HOMO level of the donor. Nevertheless, the morphology of the blend layer, as well as the non-geminated recombination can contribute to the V_{OC} origin (Potsavage *et al.*, 2009). When $J(V=0)$ and $J_{ph} \gg J_0$, the V_{OC} can be described as follow:

$$V_{OC} = n_{id} \frac{kT}{q} \ln \left(\frac{J_{ph}}{J_0} + 1 \right) \quad (3)$$

Short circuit current (J_{SC})

The J_{SC} is the maximum photo-generated current of OSCs when the applied voltage is zero (see Eq. 2). The J_{SC} directly depends on optical and electrical properties of organic semiconductors such as absorption coefficient and charge carrier mobility. J_{SC} depends on the area of the whole layer of solar cells that intersect with the active layer, thus for the J_{SC} of OSCs can be compared with the other device with similar structures, J_{SC} is obtained by dividing by the area with the unit of mA cm^{-2} . In addition, J_{SC} is related to the thickness and morphology of the organic semiconductors blend layer, light irradiation, and efficient exciton generation and dissociation (Günes *et al.*, 2007). The J_{SC} is the current output when the J_{ph} is recorded at the short-circuit condition, i.e., the condition where the output voltage bias is zero. As $V = 0$, Eq. 2 becomes:

$$J(V=0) = J_{ph} = J_{SC} \quad (4)$$

Fill factor (FF)

The FF is a parameter that measures the quality of OSCs in terms of power. FF describes how “square” the J - V curve is and it indicates how “difficult” or “easy” it is to extract photogenerated carriers from a photovoltaic device. Thus, FF can be defined in Eq. 5:

$$FF = \frac{V_{max} * J_{max}}{V_{OC} * J_{SC}} \quad (5)$$

where $V_{max} * J_{max}$ represents the maximum power (P_{max}) produced by the device. In Fig. 7, the $V_{max} * J_{max}$ is represented as a yellow rectangle (A1), while $V_{OC} * J_{SC}$ is represented as a blue one (A2). For ideal OSCs, the fill factor is 1 ($A1 = A2$), nonetheless, in real devices, it is always lower than 1 ($A1 < A2$) due to the presence of the parasitic resistance effect and the fact that photovoltaic devices are composed of p-n junction diodes, and thus J - V curve behaves more like exponential functions rather than step functions (Qi and Wang, 2013). Thus, FF can be described as:

$$FF = \frac{A1}{A2} \quad (6)$$

Power conversion efficiency (PCE)

The PCE is the main parameter of OSCs, which evaluates the capacity of a device to convert incident photons into electrons. The PCE is directly linked to the efficiency of exciton generation and dissociation, and the charge extraction efficiency. Thus, the loss mechanisms involved during these processes decrease the efficiency of the devices. The PCE can be defined by Eq. 7:

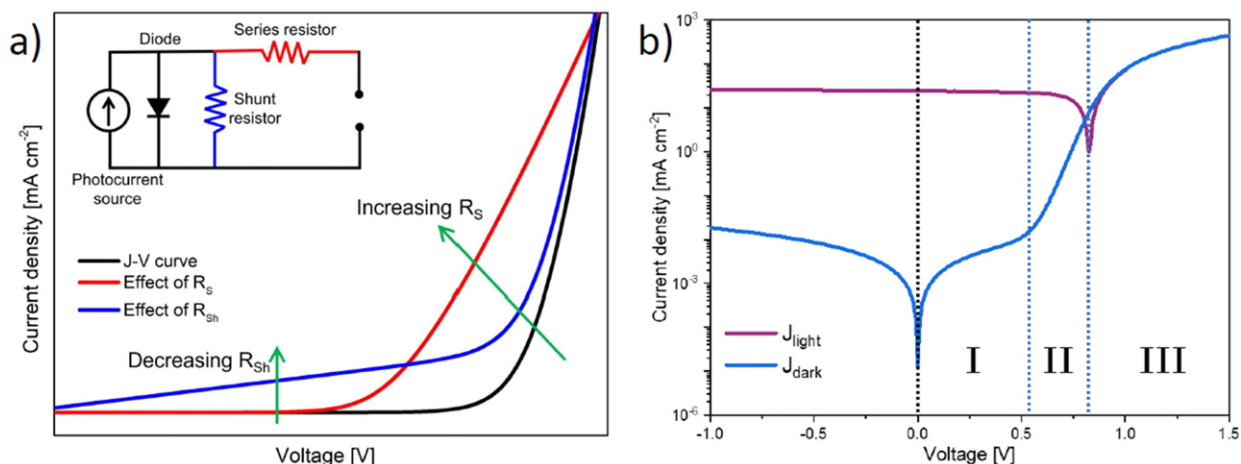


Fig. 8 (a) Effect of high R_s and low R_{sh} on the J - V characteristics of OSCs. Typical equivalent circuit of organic solar cells (inset), (b) Dark and illuminated J - V curves in a semi log scale of OSC divided into three regions.

$$PCE = \frac{P_{\max}}{P_{in}} = \frac{V_{\max} * J_{\max}}{P_{in}} = \frac{V_{OC} * J_{SC} * FF}{P_{in}} \quad (7)$$

where P_{in} is the light incident power ($P_{in} = 100 \text{ mW cm}^{-2}$ at 1 Sun AM 1.5 G).

Series and shunt resistances

In the case of practical solar cells, parasite resistances (series and shunt resistance) are non-negligible. Thus, the series resistance (R_s) and shunt resistance (R_{sh}) are counted in the equivalent model for energy losses, as shown inset **Fig. 8(a)**, where the solar cell J - V behavior can be divided into four constituent parts: a photocurrent source, diode, series resistor, and shunt resistor (Cheknane *et al.*, 2008). The R_s and R_{sh} resistances describe the current lost during the charge collection process. The R_s describes the resistance at the contacts, because of the partial energy level alignment between organic semiconductors and the metallic contacts, or buffer layers, which reduces the charge extraction. The charge carrier mobility through the organic semiconductors, as well as the thickness of the active layer, contribute to the origin of R_s . The main effect of high R_s on the OSCs performance is the less voltage drop in the diode, resulting in the reduction of FF. On the other hand, R_{sh} arises from several kinds of leakage currents originating from the pinhole in the cell, the edge of the device, or from localized defects due to the imperfections of the manufacturing process. R_{sh} has the effect of dividing current from the diode, opposite to the effect of R_s , the low R_{sh} in OSCs reduces V_{OC} and FF, resulting in the decrease of P_{out} (Nelson, 2003). The effects of the R_s and R_{sh} on the J - V characteristics of OSCs are shown in **Fig. 8(a)**. The R_s and R_{sh} can be calculated from the J - V curve slope, while the R_s is calculated at a forward voltage region higher than V_{OC} , the R_{sh} is usually calculated at the short circuit region. Considering the parasitic resistance, the equivalent circuit in **Eq. 2** can be expressed by:

$$J = J_0 \left[\exp \left(\frac{q(V - JR_s)}{nkT} \right) - 1 \right] + \frac{V - JR_s}{R_{sh}} - J_{ph} \quad (8)$$

The J - V curve is generally divided into three regions as shown in **Fig. 8(b)**. In Region I (which represents the leakage currents) the drift of charge carriers to respective electrodes is high, so no current can flow, and the J - V curve is determined by $1/R_{sh}$. In Region II (recombination currents), the J - V curve is an exponential line, and its characteristic is defined by the diode, where the diffusion current overcomes the drift current. In Region III (series resistance), the J - V curve is a second straight line with the slope controlled by $1/R_s$ where the charges start to accumulate and modify the electric field in the medium voltage (Servaites *et al.*, 2011; Waldauf *et al.*, 2006).

Organic solar cells based on semiconductor polymers

As aforementioned, OSCs are composed of two organics semiconductors: p-type organic as an electron donor and n-type as an electron acceptor. Currently, there exist several small molecules and polymers that can be used as either electron donors or acceptors that can be mixed and used them as the active layer. On one hand, OSCs based on a small molecule donor (SM_D) mixed with a polymer (P_A) or a small molecule acceptor (SM_A) showed lower efficiencies. In $SM_D:P_A$ -based OSCs, the strong intermolecular interactions and high crystallinity results in a large phase separation which limits the charge generation. Despite all small molecule OSCs ($SM_D:SM_A$) exhibiting better phase separation than that of $SM_D:P_A$ -OSCs, the similarity in the ordering packing and small domain size restricts the interpenetrated networks, resulting in inefficient charge transport pathways. However, after a great effort in morphology tuning, OSCs based on all small molecules have achieved efficiencies of up to 16% (Zhang *et al.*, 2022; Zhang *et al.*, 2022). On the other hand, devices based on a polymer donor paired with a small molecule acceptor ($P_D:SM_A$) are the most common OSCs since they are the most efficient yet. The high performance of these devices arises from the better exciton dissociation, faster charge carrier transporting, and charge recombination decrease due to a better active layer morphology

Table 1 Important milestones in the development of OSCs

Year	Milestone
2022	Tandem all organic solar cells (20.2%)
2022	Ternary organic solar cell made of two polymer donors and one NFA (19%)
2020	Single-junction polymer solar cell (18%)
2019	Single-junction polymer solar cell (15.7%)
2018	Single-junction polymer solar cell (12.7%)
2017	Tandem polymer solar cell (12.8%), Non-fullerene tandem polymer solar cell (13.8%)
2016	Non-fullerene ternary polymer solar cell (12.2%)
2015	Single-junction polymer solar cell (11.7) a-Si:PDTP-DFBT hybrid tandem cell (10.5%)
2014	Triple-junction tandem polymer solar cells (12%)
2012	Tandem polymer solar cell (10.6%)
2011	Single-junction polymer solar cell (10.1%)
2010	PTB family polymer family PCE (7.4%)
2007	PCPDTBT:PCBM solar cells (5.5%) Tandem polymer solar cell (6.5%)
2006	Polymer solar cells with inverted architecture
2005	Bulk-heterojunction P3HT:PCBM solar cell (4%–5%)
2001	Self-organized liquid crystalline solar cell of hexabenzocoronene and perylene
1995	First bulk polymer/polymer heterojunction solar cell
1993	First polymer/C60 heterojunction solar cell
1992	The photoinduced charge transfer in polymer:fullerene system is reported
1991	First dye/dye bulk heterojunction PV
1990	C60 is synthesized for the first time
1986	The first heterojunction PV device
1973	Synthesis of conductive polyacetylene

(i.e., nanoscale and vertical phase separation, crystallinity, molecular orientation, domain size, etc.). In a short span of 10 years, the efficiency of single-junction OSCs increased from 10% to over 18% (Liu *et al.*, 2020; Zhu *et al.*, 2022).

Semiconducting polymer donors

Since the discovery of conductivity in polyacetylene (Shirakawa *et al.*, 1977), a great effort in the development of semiconducting polymers has done. The new approaches were focused on synthesizing macromolecules with a conjugate backbone to overcome the disadvantages of polyacetylene: its insolubility, its difficulty processing, and it can be easily oxidization. The idea to improve the solubility of the semiconducting polyacetylene was the driving force for major research into the development of a new polymer with a conjugated backbone. Semiconducting polymers with branched side chains exhibit higher solubility than those with linear side chains of equal length and number of carbon atoms (Heintges *et al.*, 2017; Uy *et al.*, 2012). However, PSCs exhibit lower mobilities than devices based on small molecules, due to the higher molecular disorder in polymers. The newly synthesized polymers such as polypyrrole, polyaniline, poly(p-phenylene), poly(phenylene vinylene), and polythiophene revealed that the control of the polymer structures induces changes in some physical properties like the solubility and the 3D arrangement (Chiang *et al.*, 1977). Among these, the polythiophenes (PTs) stood out more than others due to exhibiting good electrical conductivity and optical properties. The electrical and optical properties of these polymers result from the delocalized electrons in the polymer backbone. Poly (3-hexylthiophene) (P3HT) is the thiophene-based semiconductor polymer most used in polymer solar cell fabrication due to its good stacking of the conjugated backbones. Some important milestones in the development of polymer-based organic solar cells are shown in Table 1.

Binary OSCs

One of the breakthroughs in the development of polymer-based solar cells was the introduction of the C60 fullerene as an acceptor material. Since then, the interest in organic solar cells based on polymer:fullerene was rapid increase due to the growing research on the development of new semiconducting polymers and C60 derivatives. Although several BHJ-blends of polymer:fullerenes were studied as active layers in PSCs, the devices based on the blend P3HT:[6,6]-phenyl-C61-butyric acid methyl ester (PC₆₀BM) exhibited the highest efficiency (~5%) (Li *et al.*, 2005; Ma *et al.*, 2005). These results encouraged research on the synthesis of new electron donor polymers with a lower band gap. However, the relatively high bandgap of P3HT (1.9 eV) restricts the photons' absorbance to wavelengths below 650 nm, and the energy levels alignment between P3HT and PC₆₀BM limits the V_{OC} of the device to 0.6 V. These issues limit the power conversion efficiency of the devices, thus, new electron donor polymers with lower band gaps and C60 derivatives were synthesized. The OSCs based on the copolymer poly [N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] and the [6,6]-phenylC71 butyric acid methyl ester (PCDTBT:PC₇₀BM) were reported with efficiencies about 6%. The PCDTBT is a copolymer with an altered structure of thiophene-benzothiadiazole-thiophene (TBT) and carbazole (Cbz) repeat units with a band gap of 1.88 eV. On the on hand, PC₇₀BM is a C60 derivative that exhibits higher photon collection due to its strong absorption in the visible range. Another example of low band gap polymer is the copolymer poly [2,6-(4,4-bis-(2-

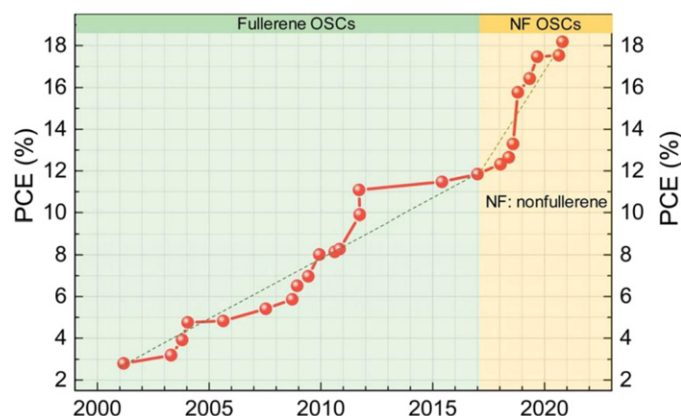


Fig. 9 Power conversion efficiency evolution of organic solar cells (data extracted from the NREL Best Research-Cell Efficiency Chart). The dashed line is a guide for the eye to show the approximate slope of efficiency increase. The figure is reproduced with permission from Jiang, P., Hu, L., Sun, L., *et al.*, 2022. On the interface reactions and stability of nonfullerene organic solar cells. *Chem. Sci.* 13, 4714–4739. Available at: <https://doi.org/10.1039/D1SC07269B>.

ethylhexyl) – 4 H-cyclopenta[2,1-b;3,4-b0]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT). This copolymer exhibits a wider spectral absorption into the infrared region than that of P3HT due to its low optical bandgap (1.5 eV). The OSCs based on PCPDTBT:PC₇₀BM were reported to yield an efficiency of ~6% (Boland *et al.*, 2010; Peet *et al.*, 2007).

Besides PCDTBT and PCPDTB, a polymer such as poly{[2,7-(9,9-bis-(2-octyl)-fluorene)]-alt-[5,5-(4,7-di-20-thienyl-2,1,3-benzothiadiazole)]} (PFDTBT), poly[(4,40-bis(2-ethylhexyl) dithieno[3,2-b:20,30-d]silole) – 2,6-diyl-alt-(2,1,3-benzothiadiazole) – 4,7-diyl] (PSBTBT), poly[2,6-(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silo-le)-alt-5,5'-(3,6-bis[4-(2-ethylhexyl) thienyl-2-yl]-s-tetrazine)] (PDTSTTz) and the fullerene derivative indene-C 60 bisadduct (ICBA), among others, were synthesized for organic solar cells applications (Yuan *et al.*, 2011; Zhang *et al.*, 2011; Zhao *et al.*, 2010). Despite the great effort made to synthesize new polymers for high-efficiency PSCs fabrication, these devices were not capable to exceed the barrier efficiency of 6%, and the first polymer solar cell with a PCE over 7% was not reported until 2010. This device was fabricated based on the polymer poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithio-phen-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophene diyl]] and the fullerene PC₇₀BM (PTB7: PC₇₀BM) (Liang *et al.*, 2010; Liang *et al.*, 2009a,b). PTB7 is a polymer based on altered units of thieno[3,4-b]-thiophene and benzo-dithiophene (BDT) with a relatively low band gap of 1.6 eV. PTB7 is the result of the structural optimization progress of the PTB-family polymers. The first devices based on a PTB-family polymer were fabricated with the poly((4,8-bis(octyloxy)benzo(1,2-b:4,5-b') dithiophene-2,6-diyl)(2-(dodecyl-oxy)carbonyl)thieno(3,4-b)thiophenediyl)) and PC₇₀BM (PTB1:PC₇₀BM), which exhibits a power conversion efficiency of 5.6%. Further PTB-based polymers (i.e., PTB2, PTB3, PTB4, PTB5 and PTB6) were developed to improve the poor solubility of PTB1 and the low V_{OC} (0.58 V) yield in devices based on it (Balderrama *et al.*, 2014; Han *et al.*, 2015). Among these, devices made of PTB4:PC₆₀BM exhibited higher V_{OC} (0.74 V) and a slightly higher PCE (6.10%) in comparison to PTB1. The differences of the physical properties among the PTB-based polymers lie on the side chains on the ester and benzodithiophene groups. After several strategies such as inverted architecture or cathode engineering with interfacial materials, the OSCs based on PTB7:PC₇₀BM reached an efficiency of over 8% (He *et al.*, 2012; MacKenzie *et al.*, 2016; Sánchez *et al.*, 2017).

These results motivated the research on the developing novel polymer donor, thus, the so-called PTB7-Th was synthesized by incorporating a 2-ethylhexyl-thiophenyl group side chain into the BDT unit in PTB7. These structure alterations led to improve the planarity and the rigidity of the polymer backbone, which results in a lower bandgap polymer donor. Thus, the V_{OC} and J_{SC} were simultaneously enhanced in OSCs based on PTB7-Th paired with PC₇₀BM that exhibited an efficiency over 10% (Balderrama *et al.*, 2018; He *et al.*, 2015; Torimubun *et al.*, 2020). Several strategies in terms of device architectures, organic and inorganic materials for the buffer layers, solution-processing methods, and the development of new donor and fullerene derivatives were considered to improve the OSCs performance. However, the efficiency of OSCs based on polymer-fullerene derivatives is limited by the fullerene's properties such as monotonous tunability of their energy levels, weak light absorption in the visible region and poor ambient stability.

To overcome these issues, several works were focused on the design and development of planar electron acceptor molecules, so-called non-fullerene acceptors (NFA). In contrast to Fullerene acceptors, the NFAs possess lower-cost synthesis, higher thermal stability, tunable bandgaps that can expand the optical absorption in the NIR region, facile tunable molecular energy levels which yield lower voltages losses and higher V_{OC}, tunable planarity and crystallinity that allow better control of the morphology of the active layer (Hou *et al.*, 2018). These advantages encouraged the rapid development of NFAs. Among the several NFAs (Armin *et al.*, 2021), the O-IDTBR, ITIC and IDIC (and some of their derivatives) were the first NFAs to yield OSCs with higher efficiencies than OSCs based on fullerene acceptors (Chen *et al.*, 2017; Guo *et al.*, 2017; Lin *et al.*, 2015; Sánchez *et al.*, 2020). The recent emergence of high-performance Y-series NFA has motivated a major revolution in the OSCs field (Li *et al.*, 2020; Moustafa *et al.*, 2022). The great interest in OSCs has arisen from the good performance of devices based on the Y-series acceptor Y6 (and its

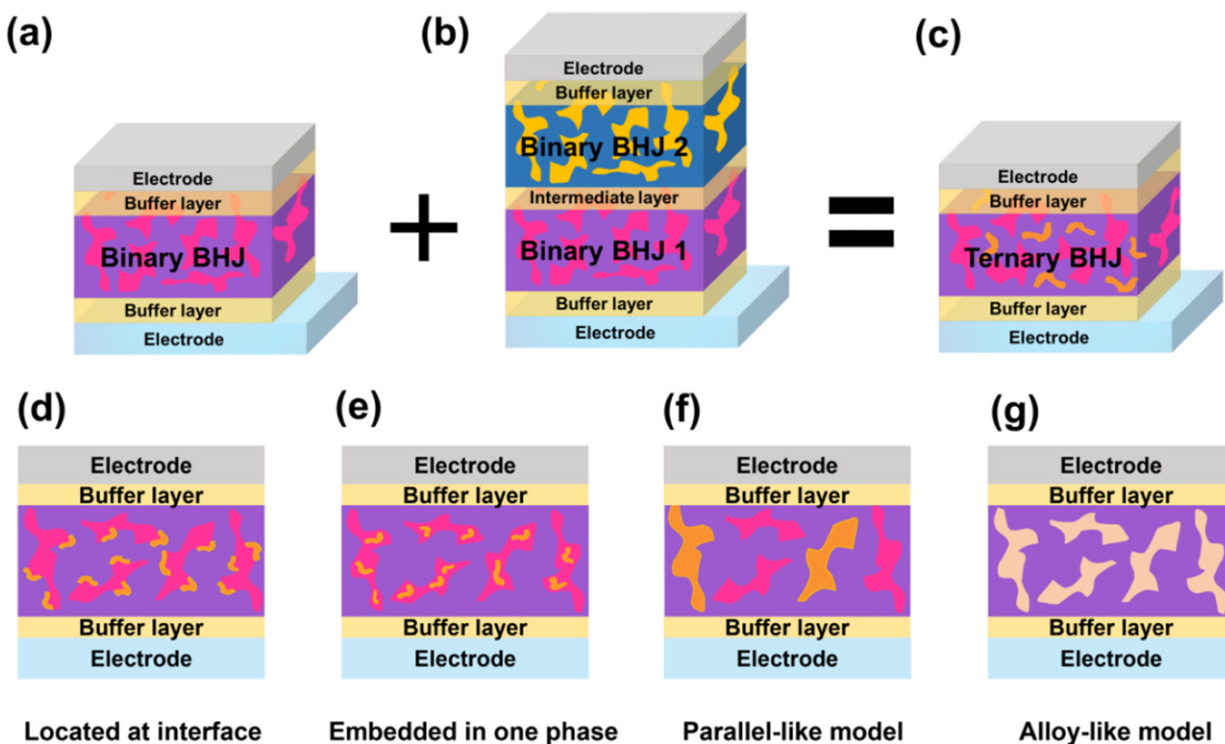


Fig. 10 Schematic of (a) bulk-heterojunction, (b) tandem, and (c) ternary OSCs. (d) – (g) Possible ternary morphologies based on the location of the third component in ternary OSCs.

derivatives) blended with the polymer donors PM6 (PBDB-T family (Zheng *et al.*, 2020)) and the D18 (and its derivatives (Jin *et al.*, 2021)) which surpassed the PCE of 18% so far (Jin *et al.*, 2021; Li *et al.*, 2021). Fig. 9 shows the evolution of the efficiency of the OSCs based on fullerene and non-fullerene acceptors.

Ternary OSCs

The development and basic concept of binary OSCs that bulk heterojunction architecture can facilitate the improvement of PCE by over 18% in single-junction devices to date, however, despite the significant advancement achieved, the PCE of OSCs has to be boosted to compete with commercial inorganic solar cells. The main limitation in OSCs is due to the intrinsic narrow absorption bands of organic semiconductor materials, making it challenging to fully utilize the energy from the solar spectrum with a single-junction binary device. To overcome the absorption limitation, ternary (multi-component) and tandem (multijunction) OSCs have become the two main strategies employed in the last decade (Fig. 10(a-c)). Tandem OSCs, despite improved light absorption as well as reduced thermalization photonic energy loss leading to a recorded PCE of over 20% reported (Zheng *et al.*, 2022), the fabrication of tandem OSCs requires complicated preparation processes, which is particularly challenging for all solution processed BHJ OSCs and may impede their commercial applications. Alternatively, the ternary strategy is not only a simple yet effective approach that can combine each merit of binary and tandem OSCs by incorporating a third component (either D or A) to improve the photon harvesting capability in a single-junction device, but also it can maintain the simplicity of single-step layer processing fabrication rather than the more complex tandem OSCs.

In principle, a ternary blend is composed of three components in a single photoactive layer: two host components consist of a primary electron donor (D or D1) and a primary electron acceptor (A or A1), together with the third guest component that is the minority addition of secondary donor, D2 or secondary acceptor, A2 into the host system. Depending on the position of the third component in the blend, it may determine the primary working mechanism of ternary OSCs (TOSCs) based on the energetic and phase structure of the third component, as shown in Fig. 10(d-g). That is, the third component can be (d) embedded in either the host donor or host acceptor phase, (e) located at the host donor/acceptor interfaces, (f) creates its phase separated from the host donor and acceptor phases forming the so-called parallel-linkage, and (g) alloyed with the host donor or host acceptor to display collective electrical properties.

However, in practice, depending on the ratio of D2 or A2 to the binary host system, the BHJ of ternary blends can feature one or more of these BHJs, and hence more than one working mechanism could be adopted. As depicted in Fig. 11, there are four main TOSCs working mechanisms proposed in the literature, (1) charge transfer and (2) energy transfer operating mechanism governed

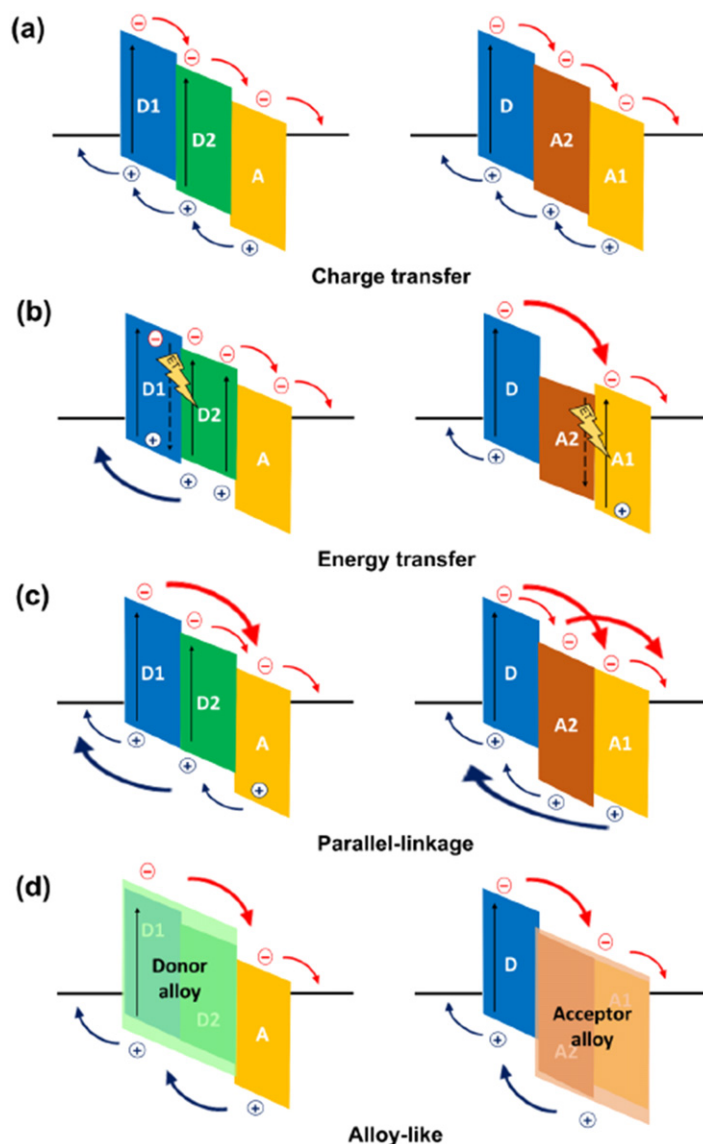


Fig. 11 Schematic diagram of four working mechanisms of TOSCs: (a) charge transfer mechanism, (b) energy transfer mechanism, (c) parallel-linkage model, and (d) alloy-like model. The left-hand side figures are D1:D2:A systems and the right-hand side figures are D:A1:A2 systems.

by the energetics, whereas (3) parallel-linkage model, and (4) alloy model operating mechanism governed by the blend phase structure.

- (1) **Charge transfer:** To obtain an efficient charge transfer, the HOMO and LUMO energy levels of the third component should be located between those of the host donor and host acceptor, forming a cascade energy alignment. This cascade energy level can avoid energy traps and can facilitate charge separation and charge transfer at the D/A interface due to the functionality of the third component as a charge relay for electron and hole transport (Fan *et al.*, 2017). In the charge transfer mechanism, the third component will directly generate free charge carriers, and the charge transport channels strongly depend on the existing host domains, indicating the location of the guest component is at the interfaces between the host donor and acceptor. As illustrated in Fig. 11(a), in the case of D1/D2/A ternary system, the exciton generated in the donor matrix (D1 and D2) could be dissociated into the charge carriers at the D1/A and D2/A interfaces. The electrons are primarily transferred to D2 through D1 before being transferred to A. Through the transport channel of A, the electrons can be effectively collected by the cathode; additionally, the holes are first transferred to D1 through D2 and then transported to the anode via the transport channel of D1, where they are efficiently gathered by the anode. Typically, the V_{OC} of the charge transfer dominant TOSCs tends to be

pinned to the smaller one of the corresponding binaries OSC devices, which may be explained by the fact that almost all the holes can reach the anode through the transport channel of the donor with a higher HOMO level.

- (2) **Energy transfer:** In a ternary blend, the other mechanism governed by the energetics of three materials is the so-called energy transfer mechanism, which sometimes can simultaneously exist with the charge transfer process. Thus, the dominant mechanism will be dependent on the kinetically competitive relationship between them. In the energy transfer mechanism (Fig. 11(b) for D1/D2/A example structure), the third component (D2) does not directly generate free carriers. Instead, D2 acts as the energy absorber to harvest energy photons from the excited energy state in D1 through Förster resonance energy transfer (FRET) or Dexter energy transfer. Then, the generated exciton in D2 dissociates at the interfaces between D2 and A, which can form free electrons and holes. The free electrons are transferred to the cathode via A's transmission channel, while the free holes in D2 can either be transferred directly to the anode or transported to D1 and subsequently to the anode via D1's transmission channel. To realize an effective energy transfer, the emission spectrum of the energy donor (D1) should overlap with the absorption spectrum of the energy acceptor (D2). Depending on the spectral gap between absorption and emission, the energy transfer mechanism mainly includes two forms: FRET (long-range and based on resonance) of electro-fluorescence and Dexter energy transfer (short-range and based on electron exchange) of electro-phosphorescence. The former occurs through the long-range dipole-induced Coulomb interaction between the energy donor and energy acceptor materials. Meanwhile, the latter primarily occurs through the electron-exchange interaction between the energy donor and energy acceptor materials. Since the radius of the energy transfer is limited, the distribution position of the energy donor and energy acceptor should be relatively near (< 10 nm), which is equivalent to the distribution requirements of the third component in the charge transfer mechanism (Zhou *et al.*, 2020).
- (3) **Parallel-linkage model:** Different from the charge transfer and energy transfer mechanisms that are governed by the energy alignment, the parallel-linkage model is one of the TOSC's fundamental mechanisms governed by the nanomorphology of the blend. This model does not necessitate complicated conditions to occur, which means that the absorption spectra, energy levels, and miscibility between the third component and the host system do not need to be perfectly matched. In the parallel-linkage model, by considering the example of TOSCs with the D1/D2/A structure, the excitons generated in each donor (D1 and D2) diffuse to the corresponding donor/acceptor interfaces and then dissociate into the free electrons and holes (see Fig. 11(c)). It is worth noting that there is no energy transfer and charge transfer between D1 and D2 because the device works independently as two sub cells (D1/A device and D2/A device) connecting in parallel, analogous to a tandem architecture. As a result, the J_{SC} of this TOSC can be equivalent to the sum of the J_{SC} values of the two individual sub cells, whereas the V_{OC} of the ternary blend lies between the V_{OC} values of two sub cells. Apart from conventional composition-dependent multi-blend systems, which only employ a limited quantity of the third component, the parallel-linkage model has a relatively high tolerance to third-component composition ratios.
- (4) **Alloy-like model:** In contrast with the parallel-linkage model, the alloy-like model usually requires the third component that has excellent compatibility with the donor or acceptor of the host system. The good miscibility between A1/A2 or D1/D2 and their similar structural backbones along with their similar electrical properties are reported to facilitate a better-intermixed phase, forming either A1/A2 or D1/D2 electronic alloy. A new charge-transfer state with a new mutual HOMO energy level and a new LUMO energy level of a new single phase of two or multiple components is formed, as shown in Fig. 11(d). As a result, the energy level changes with a variation of the third component ratio, leading to the evolution of V_{OC} in TOSCs.

The role of the third component

The judicious selection of the third component and optimization of the weight ratio in the ternary blend can play various roles in improving TOSC performance, mostly from an electrical and/or morphological standpoint. Electrically, the third component can serve as a charge-relay bridge and/or an energy transfer sensitizer for the high-energy region. Morphologically, it can induce enhanced crystallinity while maintaining the appropriate phase domain size, which is predicted to facilitate the balanced of charge dissociation and charge transport.

- (1) **Spectral and energetic modulation:** The first consideration in selecting the third component in TOSCs is guided by the requirement of extending or enhancing light absorption of the active layer, usually into near-infrared (NIR) regions or covering strong absorption in most regions of the solar spectrum. Therefore, it is a straightforward strategy to introduce a third component with complementary absorption to its host binary blend. A common method to enhance optical absorption is by synthesizing or selecting the third component material based on its optical band gap, E_g^{opt} that can extend or complement those of the host system. Generally, organic semiconductor materials can be classified into wide-, medium-, narrow-, and ultranarrow- E_g^{opt} materials, proportionate to a progressive redshift of light absorption region. The wide- E_g^{opt} materials have a light absorption in the range of 350–550 nm, like polymer donor P3HT and fullerene derivative acceptors. The medium- E_g^{opt} materials such as PDBDB-T and PBDB-TF donors can cover the spectra at 400–650 nm, while the narrow- E_g^{opt} materials such as PTB7-Th donor and ITIC acceptors have the optical absorption regions at 550–750 nm. For the ultranarrow E_g^{opt} materials like IEICO and Y-series nonfullerene acceptors, they have a low-bandgap that indicates strong optical absorptions in the NIR region. As the dissociation of the excitons primarily occurs at the D/A interfaces in the OSCs, it is necessary to choose the third component material carefully in the ternary blend to enhance charge transfer efficiency. Therefore, the third component should have an appropriate energy level alignment and offset between HOMO and LUMO of the host system to form a cascade-energy-level alignment or act as a sensitizer via an energy transfer mechanism that can enhance solar energy utilization. The small

energy offset cannot offer an adequate driving force for effective charge transfer. In contrast, if the offset is too large, it can cause unnecessary energy loss, leading to a low V_{OC} . After the excitons dissociate from the D/A interfaces, the free charge carriers are formed and transported through the electron transfer channel and hole transfer channel to the corresponding electrodes. Thus, to balance the charge transfer in the blend, a higher mobility material as an additive to the binary blend has been proposed by Liu *et al.* (Liu *et al.*, 2015). The more balanced electron and hole mobility of the device is favorable for charge transfer and collection and the utilization of excitons, thereby contributing to the improvement in the PCE of TOSCs.

- (2) **Morphological regulator:** It is well known that the photovoltaic processes of the OSCs are strongly correlated with the microstructure morphology of the active layer and thus play a critical role in determining the performance of TOSCs. An appropriate design and selection of the material of the third component can effectively adjust the phase separation scale, phase purity, and molecular packing arrangement of the different components inside the active layer. Meanwhile, the active layer with multiple subphase separations is more beneficial to the efficient separation of excitons, charge transfer, and charge collection. By fine-tuning the aggregation of molecules, the charge transfer of the TOSCs can be strongly improved, thereby enhancing the PCE of the device. Mixing a new component makes the BHJ nanostructure more complicated due to the higher complexity of the multi-materials interplay (e.g., miscibility). From the thermodynamic point of view, miscibility is a critical factor for determining the degree of phase separation in a BHJ active layer. To be specific, materials with better miscibility facilitate smaller and impure phase domains, while limited intermixing between materials tends to create a relatively purer phase with larger phase domains. The miscibility between multiple components can be quantitatively evaluated by the Flory – Huggins's interaction parameters (χ) or interfacial tension (γ) between the third component and the hosts.
- (3) **Energy loss management:** The V_{OC} is an important device parameter to consider when evaluating the performance of solar cells. In ternary OSCs, the selection of the third component with complementary absorption and suitable energy levels concerning the host binary system is a critical factor for improving J_{SC} and V_{OC} . Then, the total energy loss (E_{loss}) of photo-generated currents in devices is highly important. The E_{loss} is calculated as the difference between the minimal E_g of the materials in the blend and the qV_{OC} of the device ($E_{loss} = E_g - qV_{OC}$), where q is the elementary charge. Shockley and Quisser developed a thermodynamic detailed balance theory approach for solar cells which gives the universal V_{OC} loss. The reduced energy loss in OSCs devices based on Shockley–Quisser theory considers two main recombination losses: (1) the radiative recombination losses that are caused by the unavoidable energy losses for any solar cells ($E_g - qV_{OC}^{rsq}$) and additional radiative recombination from absorption below the bandgap ($q\Delta V_{OC}^{rad, belowgap}$), and the other is (2) the nonradiative recombination loss ($q\Delta V_{OC}^{nonrad}$), is ascribed to any type of nonradiative recombination such as trap-assisted recombination. Recently, it was reported that NFA-based OSCs exhibit efficient charge separation even though the driving force approaches zero, resulting in small $q\Delta V_{OC}^{rad, belowgap}$, encouraging us to employ the ternary strategy, especially in the case of parallel or alloy model dominant systems, where V_{OC} would be tuned with the composition loading of the third component (Jia *et al.*, 2021; Liu and Wang, 2019).
- (4) **Enhanced stability:** Generally, the stability of OSCs is affected by various factors, such as exposure to humidity and oxygen, thermal-stress-induced materials aggregation, photooxidation of BHJ active layer, and the intrinsic microstructural instability due to the spinodal demixing and/or crystallization of small molecular acceptors (Zhang and Li, 2020). The morphological instability, including so-called “burn-in”, is introduced to denote the degradation process in which the efficiencies of OSCs decline rapidly at the initial stage of the operation and then become stable afterward. The burn-in process arises from the quenching of the active layer into a non-equilibrium nanostructure during the kinetically driven solution deposition process (Gasparini *et al.*, 2019; Peters *et al.*, 2012). Severe fullerene dimerization via photoinduced free radicals often occurs in polymer–fullerene based OSCs, resulting in trap-assisted recombination due to increased photoinduced trap states and thus significantly reducing the efficiency by 25%–50% (Zhang and Li, 2020). In addition, fullerenes tend to self-aggregate upon thermal stress leading to degradation and thus poor thermal stability, while for NFA-based OSCs, negligible light-induced burn-in degradations have been reported for some specific polymer-molecule systems via replacing fullerenes by O-IDTBR and ITIC-series based small molecular acceptors (Baran *et al.*, 2018). These encouraging results point to the possibility of constructing stable ternary OSCs containing NFAs. According to recent studies, the microstructural stability of NFA-based OSCs is strongly influenced by the materials combination. Interactions among components, such as miscibility, are critical in driving microstructural degradation at a thermodynamic equilibrium state. More specifically, the poor miscibility between donor and acceptor (below the percolation threshold) would necessitate the use of additional processing optimization methods (such as thermal annealing, solvent annealing, or additives) to assist the D/A system in reaching a state above the percolation threshold that is required for efficient charge transport, although this state is far from the metastable morphology state. This kinetically quenched microstructure, however, would cause morphological deterioration, which originated from the demixing of the mixed phases toward an equilibrium state, limiting the long-term stability of OSCs devices. Furthermore, the strong crystallization of NFAs may also thermodynamically deteriorate morphological stability. Therefore, to establish stable morphology, material composites need to have a reasonable balance between miscibility and suppressed crystallization of the small molecular acceptors, which could be facilitated by adding a third component.

According to the possible combinations of three components, all the TOSCs can be classified into four categories, including polymer/polymer/small molecule, polymer/small molecule/small molecule, all-polymer, and all-small molecule types. Table 2 presents the development of the state-of-the-art ternary BHJ system from the first-time ternary strategy was introduced in 2009 to date.

Table 2 Non-exhaustive data of over a decade of research into organic ternary solar cells. Pacesetter, pivotal, record blends, *J*-*V* parameters, and respective working mechanism models. Each year, only data presenting higher efficiencies than the previous year is included, and the trend is consistent

Ternary blend	Configuration	Weight ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	Model	Year
P3HT/F8BT/PC ₆₁ BM	D1/D2/A	1/1.4/0.6	0.670	3.2	45.2	1.9	—	2009
P3HT/PCPDTBT/PC ₆₁ BM	D1/D2/A	0.8/0.2/1	0.620	8.0	55.4	2.8	CTM ^a	2010
P3HT/PC ₆₁ BM/ICBA	D/A1/A2	1/0.1/0.9	0.804	8.2	60.0	3.9	AM ^a	2011
P3HT/CuMePc/PC ₆₁ BM	D1/D2/A	01/01/2002	0.580	16.3	56.0	5.3	AM	2011
DTfBT/DTPyT/PC ₆₁ BM	D1/D2/A	0.5/0.5/1	0.870	13.7	58.9	7.0	PM ^a	2012
P3HT/aza-BODIPY/PC ₆₁ BM	D1/D2/A	0.9/0.1/1	0.560	7.9	64.7	2.8	ETM ^a	2013
PTB7/PID2/PC ₇₁ BM	D1/D2/A	0.9/0.1/1.5	0.720	16.8	68.7	8.2	CTM	2014
PTB7-Th/PID2/PC ₇₁ BM	D1/D2/A	0.8/0.2/1.5	0.780	16.7	70.8	9.2	CT/ET-M	2015
PTB7-Th/P(NDI2OD-T2)/PC ₇₁ BM	D1/D2/A	0.99/0.01/1.67	0.810	23.0	61.0	11.6	ET/PM	2016
PBDB-T/IT-M/Bis-PC ₆₁ BM	D/A1/A2	1/1/0.2	0.952	17.4	73.7	12.2	PM	2017
PTB7-Th/COi8DFIC/PC ₇₁ BM	D/A1/A2	1/1.05/0.45	0.727	27.4	73.4	14.6	AM/PM	2018
PM6/IT-4 F/Y6	D/A1/A2	1/0.24/0.96	0.844	25.4	75.9	16.3	AM	2019
PM6/3TP3T-4 F/Y6	D/A1/A2	1/0.18/1.02	0.850	26.1	75.4	16.7	CTM	2019
PM6/PC ₇₁ BM/Y6	D/A1/A2	1/0.2/1.2	0.852	25.5	76.9	16.7	PM	2020
PM6/BTP-M/Y6	D/A1/A2	1/0.24/0.96	0.875	26.6	73.5	17.0	AM	2020
PM6/DRTB-T-C4/Y6	D/A1/A2	1/0.15/1.2	0.850	24.8	81.3	17.1	CTM	2020
PM6/MF1/Y6	D/A1/A2	1.2/0.1/0.9	0.853	25.7	78.6	17.2	AM	2020
PM6/MeIC/BTP-4 F-12	D/A1/A2	1/0.12/1.08	0.863	25.4	79.2	17.4	CTM	2020
PM6/ITCPTC/Y6	D/A1/A2	1/0.06/1.14	0.861	25.7	78.8	17.4	ETM	2020
PM6/PC ₇₁ BM/BTP-eC9	D/A1/A2	1/0.2/1	0.855	26.2	77.7	17.4	CTM	2020
PM6/C8-DTC/Y6	D/A1/A2	1/0.12/1.08	0.873	26.5	75.6	17.5	CTM	2020
PM6/S3/Y6	D1/D2/A	0.8/0.2/1.2	0.856	25.9	79.2	17.5	AM	2020
PM6/Y6-1 O/BTP-BO-4 F	D/A1/A2	1/0.18/1.02	0.860	26.1	78.3	17.6	AM	2021
PM6/BTTzR/Y6	D1/D2/1	0.8/0.2/1.2	0.870	26.2	77.7	17.7	CTM/AM	2021
D18-Cl/Y6-1 O/Y6	D/A1/A2	1/0.48/1.12	0.900	25.9	76.9	17.9	AM	2021
PM6/AQx-3/Y6	D/A1/A2	1/0.4/0.8	0.870	26.8	77.2	18.0	CTM/AM	2021
PM6/BTP-S2/BO-4Cl	D/A1/A2	1/0.3/0.9	0.861	27.1	78.0	18.2	—	2021
PBDB-TF/PB2F/BTP-eC9	D1/D2/A	0.8/0.2/1.2	0.863	26.8	80.4	18.6	CTM	2021
D18-Cl/PC ₆₁ BM/N3	D/A1/A2	1/0.1/1.4	0.849	28.2	78.0	18.7	—	2021
PBDB-TF/HDO-4Cl/eC9	D/A1/A2	1/0.2/1	0.866	27.1	80.5	18.9	AM	2021
PM6/D18-Cl/L8-BO	D1/D2/A	0.7/0.3/1.2	0.910	26.66	79.3	19.2	—	2022

^aIntroduction of the working mechanism. CTM is the abbreviation of the charge transfer mechanism, ETM is the electron transfer mechanism, AM is an alloy-like model, and PLM is a parallel-linkage model.

Note: Reproduced from Doumon, N.Y., Yang, L., Rosei, F., 2022. Ternary organic solar cells: A review of the role of the third element. *Nano Energy* 94, 106915. Available at: <https://doi.org/10.1016/j.nanoen.2021.106915>.

Future Directions

In the last 5 years, the efficiency of organic solar cells has rapidly grown to almost reach the 20%. Higher efficiencies are expected in the next few years from further improvements in non-fullerene acceptors, complementary absorption of the acceptor and donor, a suitable energy level between donors and acceptors, and appropriate blend morphology. Also, we need to reduce the use of toxic reagents and develop new technological processes based on eco-compatible solvents to minimize the environmental impact and reduce the costs of fabrication. The long-term stability of OSCs is one of the main drawbacks which limit their applications and commercialization, and the improvement of the device's stability has become a big challenge. The introduction of additives and interfacial layers and new materials for encapsulation has improved the lifetime of the OSC, but this is not enough, and more research is needed for example to understand the effects of the blend morphology on the device stability under real operando conditions. In this sense, the stability has to be investigated under different atmospheric, types of illumination (i.e., indoor or low-light illumination), and thermal conditions. Another important point to be considered to commercialize OSC is the active area. Major works on OSC are based on small areas of one or few mm^2 and there are few reports on large areas. It is well known that efficiency is minor in large areas and new engineering strategies have to be developed to keep high efficiencies and long-term stabilities. Currently, various scalable fabrication techniques have been proposed for large-area OSC, such as screen printing, brush coating, gravure printing, slot-die coating, knife coating, pad printing and flexographic printing. However, the issue is not solved, and new and more accurate processes and fabrication methods have to be established.

Finally, the OSC has revived interest in its versatility and applications, which has opened the door for future directions of the development of transparent and flexible devices focused on indoor applications, the internet of things and buildings.

Conclusion

The evolution of the organic solar cells' performance over time has been addressed in this article. Since the discovery of photovoltaic effects in an organic semiconductor, the development of new molecules has been one of the main targets of research in this field. The novel donor and acceptor materials should not only own good optical and electrical properties, but also have the capability to control the morphology of the blend (e.g., vertical phase segregation of donor and acceptor with domains on the nanoscale, structural packing, and orientation) determined by their crystallinity, molecular packing, solubility, miscibility, and segregation behavior. Ternary OSC is a useful strategy to improve the efficiency of organic photovoltaics in which the third component plays a key role in the morphological control of the blend. The accurate selection of the third component aside from different factors (such as solvent additives, thermal or solvent annealing, etc.) results in a blend morphology that enables to improve the exciton dissociation and the free charge carrier transport and reduce the recombination losses, yielding higher PCE. So far, the efficiency of organic solar cells has been boosted near to 20%, which set this photovoltaic technology to compete with its counterpart inorganic solar cells.

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Flexible Electronics

Qianqian Shi, Dapeng Liu, and Jia Huang, Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Shanghai Institute of Intelligent Science and Technology, Tongji University, Shanghai, PR China

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Abstract

During the fast development of the human financial society, enormous efforts have been made in the development of the advanced electronic devices for flexible systems and electronic skin (e-skin). Among various kinds of materials, low-dimensional nanostructured materials and organic materials, are considered as the suitable candidates for the manufacturing of the flexible electronics, with the advanced properties of the flexibility, facile processability, relatively low cost, stretchability, environmental sensitivity. Therefore, the flexible devices and integrated systems will be the basic units for the development of the future artificial intelligence and human-body enhanced systems. In this article, the recent researches in flexible electronics, including materials design and flexible sensors, are reviewed and discussed. The following applications of the integration of the functional flexible devices for e-skin systems are presented. Finally, the main challenges and the future research are purposed.

Key Points

- The chemistry and structure design for the flexible materials.
- The device structure and functions of the flexible electronics.
- The integration and applications in the electronic skins.
- The challenges, issues, and outlooks for next-generation e-skin and artificial intelligence.

Introduction

When we talk about integrated circuits and computers, we mostly think about the hard chips made from silicon. Considering the development of the healthy monitoring, human body enhancement, and smart life, novel and advanced electronics are coming into our daily life and society. Quite different from the silicon-based electronics, the future flexible electronics are portable, wearable, and implantable. New materials and fabricating technologies are being investigated and developed to achieve the requirements of the bio-safe and wearable functional electronic products ([Heremans et al., 2016](#); [Liu et al., 2017](#)).

This article will start with the issues and the key parameters towards the flexible device and integrated systems. After that, the insight of the advanced materials as the key components for substrates, semiconductors, conductors, and encapsulations will be proposed. The following design and the chemistry to control the material properties are discussed. Practical flexible electronic is a complex system. Novel fabricating strategies for using new materials need to be further investigated. Finally, the currently reported demonstrations are presented before the conclusion.

1. Flexible Materials for Electronics

- 1.1. Conductors
- 1.2. Semiconductors
- 1.3. Substrates

2. Flexible Sensors

- 2.1. Tactile Sensors
- 2.2. Chem-/Bio- Sensors
- 2.3. Additional Properties

3. Highly-integrated E-skin

4. Summary and Outlook

Flexible materials for electronics

In the past decades, many advanced materials with flexibility and stretchable ability have been developed. As electronic materials and devices are becoming portable, wearable, and implantable for future smart life. Materials chemistry plays an essential role in the exploration of flexible materials design, synthesis, and the combination of the soft materials with active conductive/semi-conductive materials. Developing novel materials nanostructure and materials integration design have been purposed and investigated ([Hammock et al., 2013](#)).

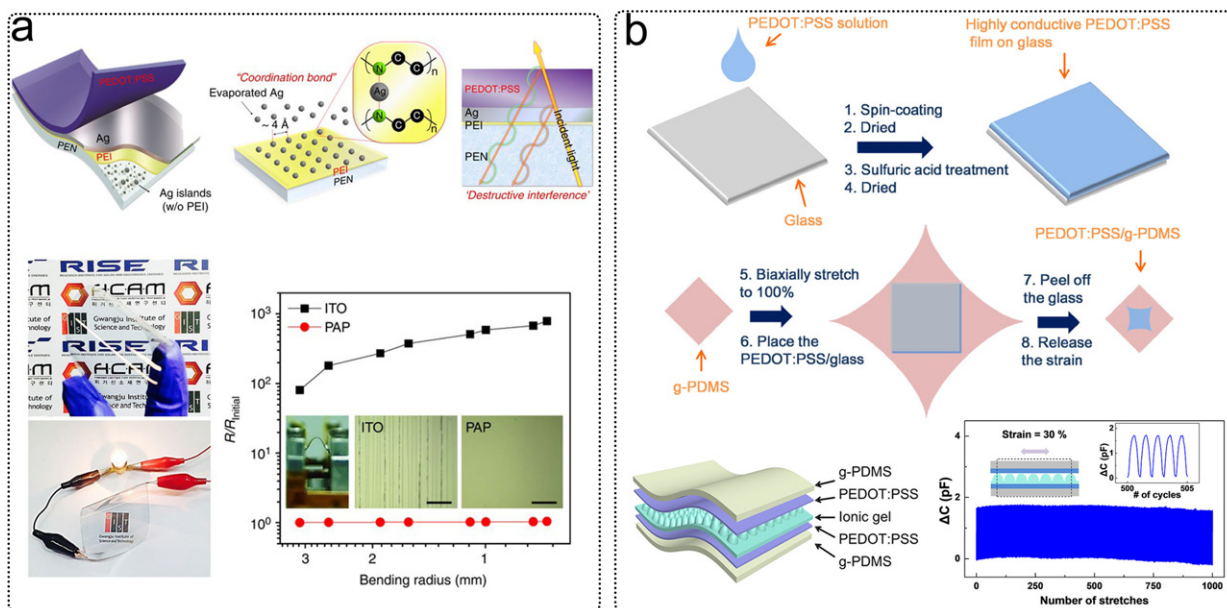


Fig. 1 (a) Schematic diagram of the PEDOT:PSS-Ag-PEI (PAP) electrode, the growth mechanism of the Ag film, the large-area flexible PAP, the change of the resistance versus the bending radius of the flexible PAP (black) and ITO (red) electrodes on the PEN substrate. (b) Schematic diagram of the fabrication of PEDOT:PSS/grafted-PDMS and the structure of the electrode, the sensor structure based on the electrode, the capacitance signal over 1000 stretching cycles to 30% strain. Reproduced from Kang, H., Jung, S., Jeong, S., Kim, G., Lee, K., 2015. Polymer-metal hybrid transparent electrodes for flexible electronics. *Nat. Commun.* 6 (1), 6503. Copyright 2015, Nature Publishing Group. Li, G., Qiu, Z., Wang, Y., *et al.*, 2019. PEDOT:PSS/Grafted-PDMS electrodes for fully organic and intrinsically stretchable skin-like electronics. *ACS Appl. Mater. Int.* 11 (10), 10373–10379. Copyright 2019, American Chemical Society.

For the fabrication of flexible electronics, stretchable systems, and electronic skin (e-skin), three basic components are important to construct electronic units, including conductors, semiconductors, and substrates/dielectrics. The relative materials have been developed for flexible field-effect transistors (FETs), flexible light-emitting diodes (LEDs), flexible solar cells, which are utilized to build functional electronic systems (Wang *et al.*, 2015).

In this section, the material design chemistry and the major advances of the flexible and stretchable materials applied as conductors, semiconductors, and substrate/dielectric are reviewed and discussed.

Conductors

Conductors are playing an essential role in the connection of the electronic units, such as transistors, resistors, capacitors, and cells, which are unified for the construction of logic circuits and functional electronics. Many flexible conductive materials and hybrid materials can be applied as flexible and stretchable conductors. Among traditional metal electrodes, gold (Au), silver (Ag), and copper (Cu) have been widely researched in silicon-based electronics and integrated circuits. Nano-engineering materials exhibit novel mechanical and optical properties, which have been investigated in flexible optoelectronic applications (Kamyshny and Magdassi, 2019).

Organic materials have been explored for flexible devices. For example, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) exhibits visible-range optical transparency, electrical tunability, high flexibility, and stretchability. The performance of electricity, stability, and mechanical properties of PEDOT:PSS can be controlled and optimized by solvents, acids, ions, and polymers. It was widely used in the fabrication of displays, photovoltaics, and functional transistors, as the transparent flexible electrodes, active channels, and interconnectors (Crispin *et al.*, 2006; Fan *et al.*, 2019).

PEDOT:PSS is a water-soluble conductive material. It is facile to design and develop the hybrid functional materials based on PEDOT:PSS. Zhu *et al.* demonstrated a transparent stretchable supercapacitor based on the hybrid electrodes, which consist of the PEDOT:PSS and silver nanowires. The supercapacitor displays a certain degree of transparency and stretchability with stable capacitance. To improve the elastic properties and the possibility in the e-skin applications, Kang *et al.* designed a polymer-metal (PEDOT:PSS-Ag) hybrid electrode with a high visible-light transmittance $> 95\%$, a low sheet resistance $< 10 \Omega \text{ sq}^{-1}$, and a small bending radius $< 1 \text{ mm}$, showing promising applications in polymer solar cell and an organic light-emitting diode (Fig. 1a) (Kang *et al.*, 2015). Li *et al.* demonstrated PEDOT:PSS/grafted-PDMS bilayer electrodes to enhance the stretchability of the device and the operation stability (Fig. 1b) (Li *et al.*, 2019).

Conductive nanowires provide potential applications in flexible and transparent electrodes, such as silver and copper nanowires. Metal nanowires can be easily and uniformly dispersed in the solvent, which can be solution-processed and patterned via blading and printing methods. Due to the great extensibility of metal, the metal nanowires exhibit excellent flexibility and bending

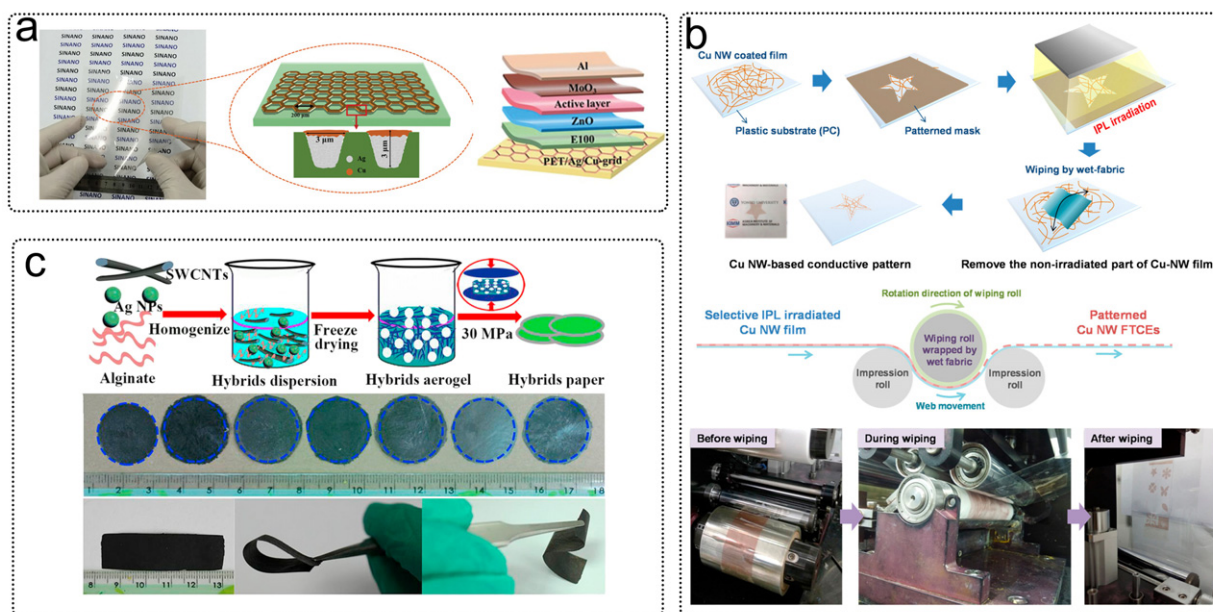


Fig. 2 (a) Photograph and the schematic diagram of the large-area PET/Ag/Cu electrode, the device structure of the solar cell based on the PET/Ag/Cu electrode. (b) Schematic illustration of the patterning method for Cu NW FTCEs using a mask for selective IPL irradiation. (c) Fabrication schematic of the SWCNTs/Ag NPs/alginate hybrid paper with folded structure, photographs of various SWCNTs-based hybrid papers, photographs of the SWCNTs/Ag NPs/alginate hybrid paper under diverse mechanical deformation. Reproduced from Han, Y., Chen, X., Wei, J., *et al.*, 2019. Efficiency above 12% for 1 cm² flexible organic solar cells with Ag/Cu grid transparent conducting electrode. *Adv. Sci.* 6 (22), 1901490. Copyright 2019, Wiley-VCH. Zhong, Z., Lee, H., Kang, D., *et al.*, 2016. Continuous patterning of copper nanowire-based transparent conducting electrodes for use in flexible electronic applications. *ACS Nano* 10 (8), 7847–7854. Copyright 2016, American Chemical Society. Zhao, S., Gao, Y., Li, J., *et al.*, 2015. Facile preparation of folded structured single-walled carbon nanotube hybrid paper: Toward applications as flexible conductor and temperature-driven switch. *Carbon* 95, 987–994. Copyright 2015, Elsevier Publishing Group.

durability. Their mechanical properties can suit well with the bending, twisting, and stretching requirements of flexible electronics. Furthermore, the diameter of the metal nanowire under hundreds of nanometers allows the transmission of visible light, which reveals that metal nanowires are promising materials for the design of highly transparent electronics. Silver nanowires have been extensively studied as transparent and flexible electrodes for high-performance solar cells, organic transistors, and organic light-emitting diodes (Jin *et al.*, 2018a; Lee *et al.*, 2017; Xue *et al.*, 2017).

Besides the direct utilization of the silver nanowires as the electrodes for flexible and transparent devices, silver nanowires (Ag NWs) can be uniformly dispersed and facilely mixed with other functional materials. The Ag NWs/poly(urethane acrylate) (PUA) layer was developed for stretchable solar cells. The dispersed Ag NWs solution is suited well with the polymer film fabrication process for thermal sensing and pressure sensing applications. For the enhancement of the Ag NWs-based composite materials, Han *et al.* developed a highly conductive and transparent grid based on composite Ag/Cu with high visible light transparency of 84% and a sheet resistance $< 1 \Omega \text{ sq}^{-1}$. The organic solar cell based on the advanced electrode exhibits a high efficiency of 12.26% for 1 cm². The modification of the PEDOT:PSS with ZnO buffer layer was utilized to achieve further high performance (Fig. 2a) (Han *et al.*, 2019).

Similar to the advanced properties and flexible electronic application of Ag NWs, other metal-based nanomaterials have also been studied by many researchers. Copper (Cu) is a relatively low-cost conductive material compared with Ag. Zhong *et al.* investigated the Cu nanowires via simple, low-cost, and scalable patterning methods (roll-to-roll). The Cu nanowires were applied into a phosphorescent organic light-emitting diode (PhOLED) and a conductive heater. Other metal nanocomposites such as Cu nanoparticles and gold (Au) grids have been developed in flexible optoelectronic devices (Fig. 2b) (Zhong *et al.*, 2016).

Other low-dimensional inorganic materials, such as nanostructured metal, carbon nanotubes (CNTs), and graphene, have great physicochemical properties, high hole/electron mobility, and mechanical strength, which can be applied as conducting layers in field-effect transistors (FETs) and sensors. CNTs and graphene are promising materials as bottom electrodes for vertical FETs without electromagnetic shielding ability. In addition, CNTs can be well-dispersed in the solution with surfactants as printable inks, which can be applied in the large-scale and patterned printing process (Luo *et al.*, 2018; Yu *et al.*, 2011).

CNTs and graphene were extensively studied as the flexible and transparent electrodes in solar cells. CNTs can suit well in the solution processing route with other functional materials. Jung *et al.* reported the CNTs with PDMS wrapping layer, which was developed for stretchable tensile sensing applications. Zhao *et al.* purposed the hybrid paper electrodes based on the single-walled CNTs (SWCNTs), Ag nanoparticles (Ag NPs), and alginate. The conductive paper exhibits great stability under various operating conditions (Fig. 2c) (Zhao *et al.*, 2015).

Semiconductors

Semiconductors are the active components to add functionalities, which is critical for the construction of the flexible device. Organic semiconducting small molecules and polymers are the naturally pliable materials with their intrinsically low elastic modulus in flexible devices. The widely researched small molecules include C₈-BTBT, PCBM, DNIT, and TIP-pentacene. More kinds of semiconducting polymers have been used in the flexible electronic fabrication, such as P3HT, DPP-based polymers, PCDTPT, IDT-BT, PNDI-2 T, and PBDTTT-based polymers (Wakayama and Hayakawa, 2019; Ling *et al.*, 2018; Shin *et al.*, 2014).

Organic semiconductors (OSC) can be deposited on the flexible substrates by various methods (thermal evaporation, spin coating, printing, blading) for high-performance flexible OFETs, OLED, and organic solar cells. The OSC-based flexible FETs display promising applications in pressure sensing, magnetic sensing, nonvolatile memory, multiplexed diagnostics, and stretchable healthcare electronics (Someya *et al.*, 2010). For the practical application in e-skin, the organic device with only flexible properties maybe not enough for the requirement of the e-skin. The stretchability can be added to the OSC polymer via chemical structure modification. Mun *et al.* purposed a simple and general molecular design strategy based on the chemical structure of the OSC polymer. Two types of co-monomer units were incorporated which would reduce the crystallinity and longer-range orders. The optimized OSC polymer can maintain high mobility and have improved stretchability with promising mechanical reversibility. The general molecular design strategy provides a facile way to develop high-performance stretchable OSC polymers (Fig. 3a) (Mun *et al.*, 2021).

Besides OSC molecules, low-dimensional materials, such as CNTs, have been widely developed for flexible devices. The electrical properties of CNTs can be tuned by changing the layer number (single-walled carbon nanotubes and multi-walled carbon nanotubes) and the combinations of N and M (structural parameters which indicate how the carbon nanotube is twisted). Therefore, the semiconducting CNTs can be obtained as the conducting layer in flexible devices. Similarly, the semiconducting CNTs can also be applied in the facile solution-processed technique, such as ink-jet printing and roll-to-roll printing on flexible substrates (Shin *et al.*, 2016; Park *et al.*, 2013). The CNTs-based device on flexible substrates have been investigated for the neurological skin, memory system, and pressure sensor. Nela *et al.* demonstrated a flexible 16 × 16 CNT TFT array with low operation voltage and faster response than human skin (<30 ms). Graphene is another highly conductive material with great air stability and excellent mechanical properties, which has been studied in the stretchable and multimodal e-skin (Fig. 3b) (Nela *et al.*, 2018).

Stretchable property is the key performance for the future development of the advanced wearable devices and e-skin. Intrinsic stretchability provides a lot of advantages, which include high-device density, high-data fidelity, and excellent mechanical robustness. Designing the hybrid materials or bilayer materials based on conventional high-performance semiconducting polymer (PEDOT:PSS, P3HT, PQT-12, etc.) and elastic polymer (PDMS, SEBS, PU, etc.) is a promising route for stretchable organic transistors and further stretchable electronics (Xu *et al.*, 2019, 2017). Choi *et al.* have demonstrated a unique hybrid stretchable semiconducting polymer (P3HT) with elastic polymer (PDMS) via a simple solution blending method to achieve charge carrier mobility and stretchability improvement. The hybrid polymer was compared with the bilayer structured polymer (P3HT/PDMS) and pristine P3HT. The blended polymer maintains the mobility under a strain up to 100% without crack observed (Fig. 3c) (Choi *et al.*, 2016). Another promising route is the introduction of the soft segments to design advanced novel semiconducting polymers, which can enhance the polymer chain flexibility and dynamic interactions. This part has been reviewed and discussed above.

Substrates

Commercial polymers (polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinyl pyrrolidone) (PVP), polyimide (PI), poly(ethylene terephthalate) (PET), etc.) are promising candidates with their intrinsic flexibility, which have been investigated as the flexible substrates for wearable electronics. PET and PI are the commonly used materials to fabricated flexible electronics due to the advantages of low cost, great durability, and high transparency. PMMA, PS, and PVP can be facilely deposited on PET or PI substrate via solution-processing approach as the flexible dielectric. Many natural polymers such as cellulose, chitosan, and starch, have been applied as the self-standing flexible substrate (Li *et al.*, 2016; Ren *et al.*, 2016; Choi *et al.*, 2018). Shi *et al.* purposed a flexible, printable, synaptic electronic with ultralow-power consumption based on quantum dots and OSC with poly(ethylene naphthalate) (PEN) substrates. The device shows stable light-induced synaptic performances under bending conditions, which exhibits further potential applications in flexible smart e-skins and artificial intelligence (Fig. 4a) (Shi *et al.*, 2021).

Other functional polymers such as PVDF-based polymers and ionic electrolyte polymers with free-standing properties also have been widely researched in the applications of flexible devices (Li *et al.*, 2020; Sun *et al.*, 2015). The PVDF-based polymers with force-sensitive ferroelectricity are soluble which can be processed via various methods (electrospinning and spin coating) for flexible nanogenerators, tactile sensors, and strain sensors. Ionic electrolyte polymer is a key material in ionic battery and low-power devices. Organic ionic pairs can be used with stretchable polymer for the facile fabrication of stable ionic chemiresistor (Jin *et al.*, 2018b). Tempo-treated nanocellulose is a widely-studied natural polymer, displaying widespread application in energy, construction, and electronics. Dai *et al.* demonstrated an environmental-friendly cellulose nanopaper with high capacitance and self-standing ability in the application of low-voltage organic transistors. The high performance of the OFETs is mainly from the intrinsic ionic conductivity of the cellulose nanopaper, revealing the natural ionic film can be considered as the high-capacitance dielectric for transparent, flexible, and low-voltage electronics (Fig. 4b) (Dai *et al.*, 2018).

Stretchable insulating polymer is a kind of essential material for advanced wearable devices and electronic smart skins. Elastic polymers such as PDMS and SEBS were extensively studied as the stretchable substrate or dielectric layer (Xu *et al.*, 2017). Organic semiconducting polymers (P3HT, DPP-based polymers) or semiconducting CNTs can be easily deposited on the elastic dielectric to construct the stretchable devices. OSC polymers and PDMS is facile in nanoengineering via patterned coating, printing, blading, and electrospinning.

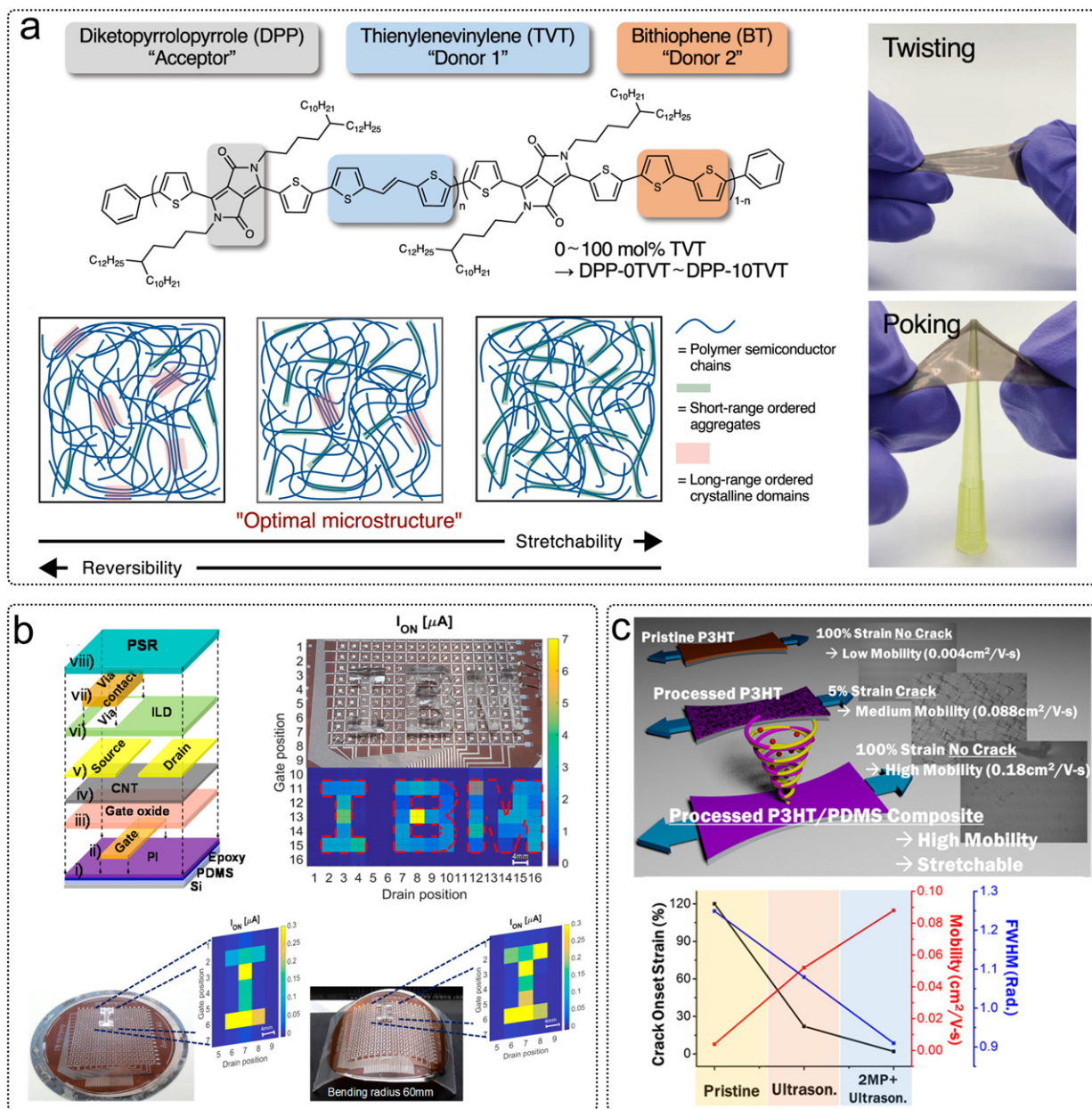


Fig. 3 (a) Molecular design and properties of stretchable terpolymers, based on the TVT unit, microstructures of polymer semiconductors that are ideal for stretchability and mechanical reversibility, photographs of the fully stretchable transistors under various mechanical deformations. (b) Schematic of the process flow for the flexible pressure sensor, current mapping of CNT TFT active matrix showing the pressure sensing of "IBM" logo made by PDMS, comparison of pressure sensing on the flat and curved surfaces with a bending condition. (c) Schematic diagram of the designed elastomer-polymer semiconductor blends, crack onset strain, full width half max of respective GIXRD spectra, and hole mobility of P3HT films fabricated from pristine, 2 min ultrasonicated, and 15 vol% 2-methylpentane added then 2 min ultrasonicated P3HT solutions. Reproduced from Mun, J., Ochial, Y., Wang, W., *et al.*, 2021. A design strategy for high mobility stretchable polymer semiconductors. *Nat. Commun.* 12 (1), 3572. Copyright 2021, Nature Publishing Group. Nela, L., Tang, J., Cao, Q., Tulevski, G., Han, S.-J., 2018. Large-area high-performance flexible pressure sensor with carbon nanotube active matrix for electronic skin. *Nano Lett.* 18 (3), 2054–2059. Copyright 2018, American Chemical Society. Choi, D., Kim, H., Persson, N., *et al.*, 2016. Elastomer-polymer semiconductor blends for high-performance stretchable charge transport networks. *Chem. Mater.* 28 (4), 1196–1204. Copyright 2016, American Chemical Society.

Schwartz *et al.* used the patterned PDMS with nanostructure as elastic dielectric to design flexible polymer transistor. The device exhibits high-pressure sensitivity, which was applied in e-skin and human health monitoring. Flexible and stretchable polymer-based hybrid component structure design is another promising route for functional and performance-optimized electronics (Schwartz *et al.*, 2013). Kang *et al.* presented a stretchable polymer fabricated by cross-linking reaction between the liquid reactive rubber and cross-linking agent, which consists of hard segments of the nanocrystals and soft rubber segments. The stretchable P3HT OFET based on the cross-linked dielectric can be operated stably under the stretching of $\epsilon \leq 34\%$ (Fig. 4c) (Kang *et al.*, 2018).

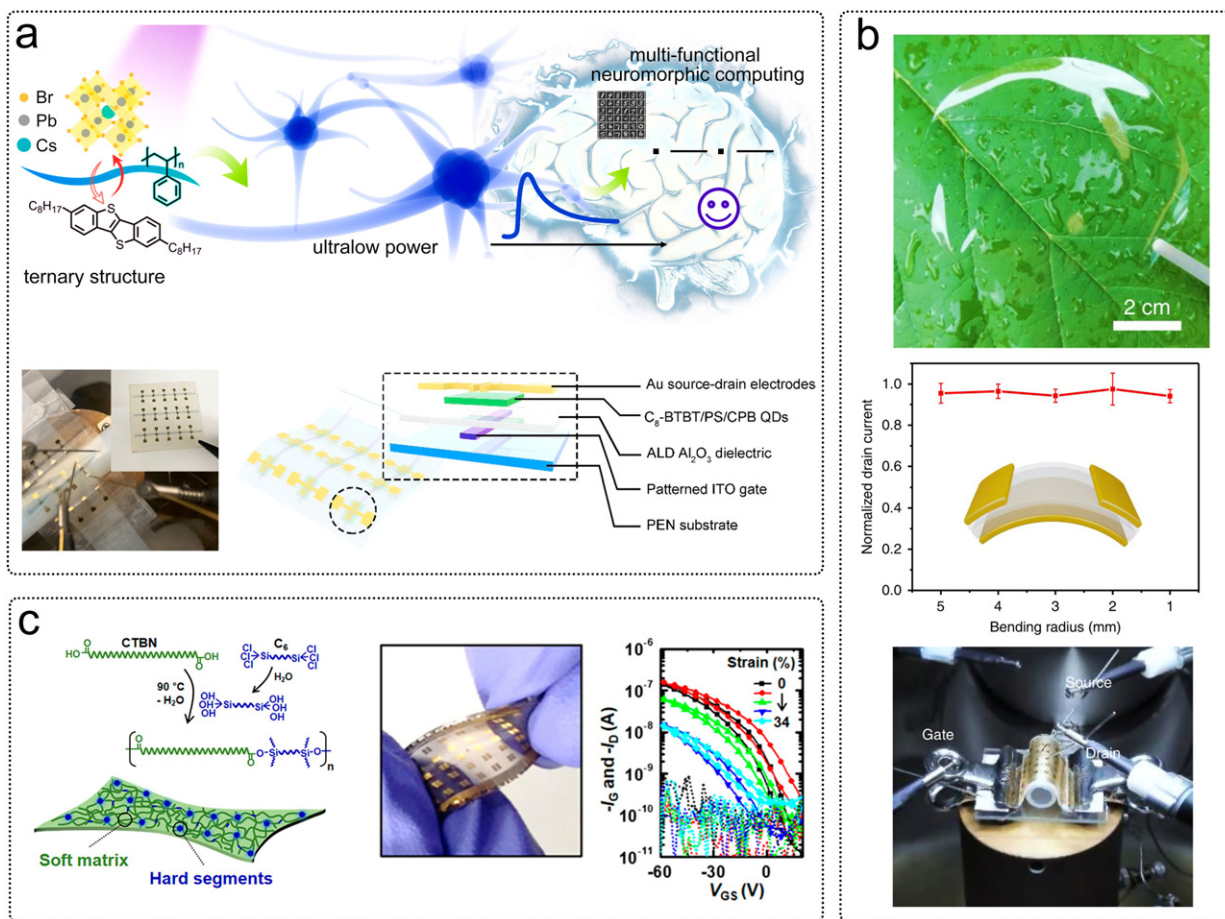


Fig. 4 (a) The chemical structure of perovskite quantum dots, PS and C₈-BTBT for multifunctional neuromorphic simulations, the photo image of the flexible device tested under bending state and the schematic illustration of the 3×3 device on the flexible substrate. (b) Photographs of the ion-conductive cellulose nanopaper (ICCN), bending tests on flexible ICCN-based OFETs, the photographs of the bending test. (c) Chemical structure of CTBN and C₆ and the scheme to form segmented elastomeric network film by a cross-linking reaction, the photograph of the structure of a fully stretchable OTFT achieved using the cross-linked CTBN GD, transfer curves with various strain. Reproduced from Shi, Q., Liu, D., Hao, D., *et al.*, 2021. Printable, ultralow-power ternary synaptic transistors for multifunctional information processing system. *Nano Energy* 87, 106197. Copyright 2021, Elsevier Publishing Group. Dai, S., Chu, Y., Liu, D., *et al.*, 2018. Intrinsically ionic conductive cellulose nanopapers applied as all solid dielectrics for low voltage organic transistors. *Nat. Commun.* 9 (1), 2737. Copyright 2018, Nature Publishing Group. Kang, B., Song, E., Lee, S.B., *et al.*, 2018. Stretchable polymer gate dielectric with segmented elastomeric network for organic soft electronics. *Chem. Mater.* 30 (18), 6353–6360. Copyright 2018, American Chemical Society.

Flexible Sensors

The final goal of the development of the flexible electronics is to create an artificial skin with human-like sensory capabilities, which can be applied with multi-sensory surfaces for autonomous artificial intelligence and medical diagnostics. E-skin sensors with self-power supply mimicking the human physical and chemical signal receptors have been intensively studied, which are expected to be applied and integrated into future smart skin systems and human-machine interfaces for health monitoring, emergency aid, and robot development. For the enhancement of the practical applications, the e-skin devices should have excellent mechanical deformability and high-level device integration, as well as stable stimuli response and signal transmission during the deformations of the devices (Ho *et al.*, 2016; Tee *et al.*, 2012).

For the construction of the e-skin, high-performance physical and chemical sensing devices, and power supply devices are key components and in high requirement. In this section, the sensory device, self-power electronic, and functional e-skin were reviewed and discussed.

Tactile Sensor

Artificial intelligence and smart robots have shown enormous utility in the efficiency enhancement and the cost reduction in the industrial manufacturing. For the robotic design that can work and respond appropriately by collecting environmental information, highly functional tactile sensors and array systems are required to improve the sensing speed and the stability of the signal

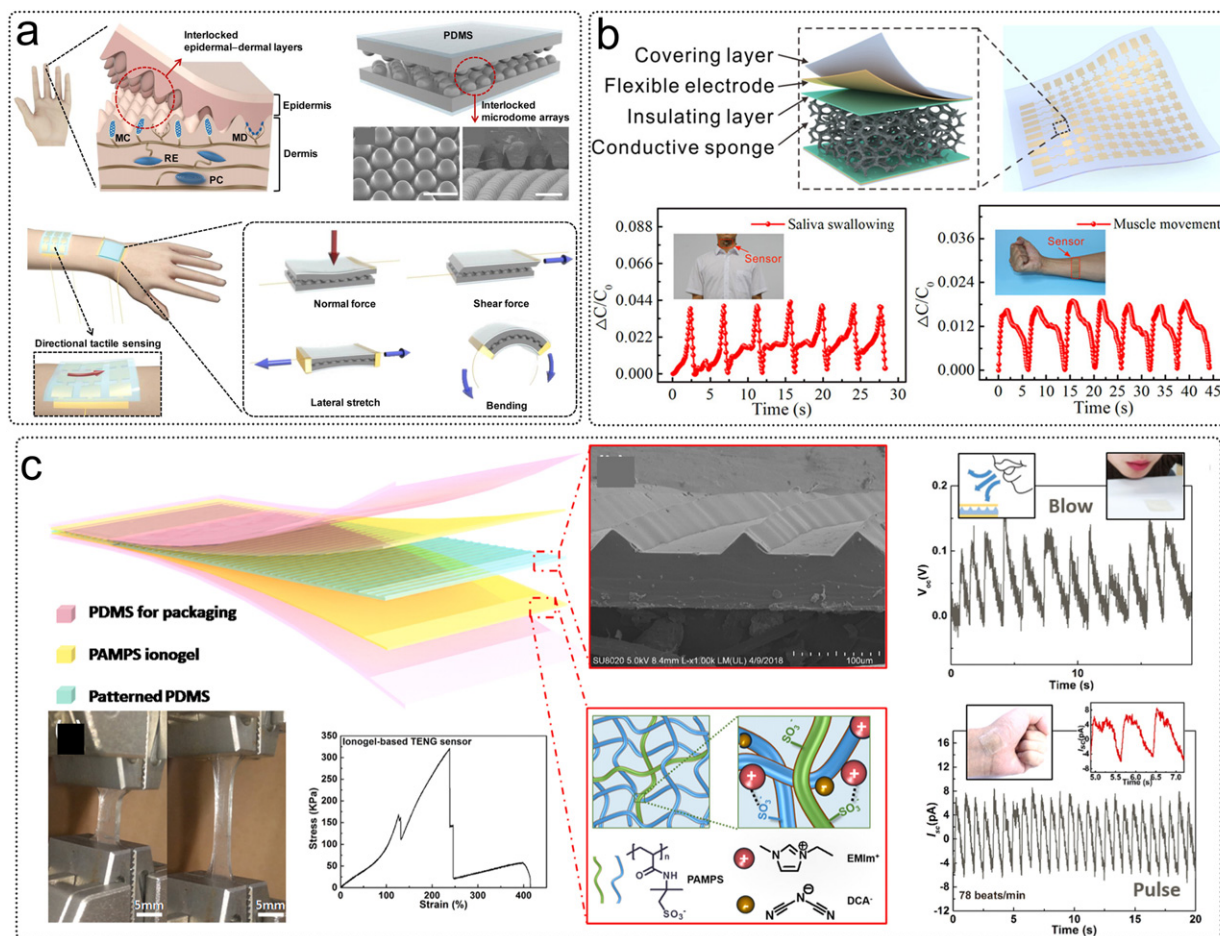


Fig. 5 (a) Electronic skin based on CNT-PDMS composite films with interlocked microdome arrays. (b) Schematic illustration of the highly capacitive tactile sensors based on the microcellular dielectric layer, real-time detection of a healthy adult male. (c) Structure of the transparent and stretchable TENG-based tactile sensor, the self-powered sensor could detect air flow and the human pulse beats. Reproduced from Park, J., Lee, Y., Hong, J., *et al.*, 2014. Tactile-direction-sensitive and stretchable electronic skins based on human-skin-inspired interlocked microstructures. *ACS Nano* 8 (12), 12020–12029. Copyright 2014, American Chemical Society. Qiu, J., Guo, X., Chu, R., *et al.*, 2019. Rapid-response, low detection limit, and high-sensitivity capacitive flexible tactile sensor based on three-dimensional porous dielectric layer for wearable electronic skin. *ACS Appl. Mater. Int.* 11 (43), 40716–40725. Copyright 2019, American Chemical Society. Zhao, G., Zhang, Y., Shi, N., *et al.*, 2019. Transparent and stretchable triboelectric nanogenerator for self-powered tactile sensing. *Nano Energy* 59, 302–310. Copyright 2019, Elsevier Publishing Group.

transduction. To measure the magnitude of the tactile stimuli, the pressure signal should be converted into the electrical signal. Various transduction mechanisms have been extensively investigated based on different facile readout mechanisms (Yamada *et al.*, 2011).

The first-type sensor is based on the piezoresistivity mechanism, which would transduce the change of the device resistance into the measurement of the strain. The geometry of the sensing layer, the band structure of the semiconductor, the contact resistance, and the inter resistivity of the sensing composite could induce the change of the device resistance. Conductive nanostructured materials can be easily obtained via nanoengineering methods such as electrospinning and nanopatterning. To achieve the stretchable properties with maintaining the conductivity. The conductive nanocomposites can be incorporated with elastic polymer or nanoflexible materials. Park *et al.* demonstrated a wearable and stretchable device based on the thin films of the CNT-PDMS composite films. The PDMS nanostructure (interlocked microdome arrays) was patterned inspired from the human skin. The CNT-PDMS film based electronic array exhibits highly sensitive detection capabilities to various mechanical stimuli (shear, stretch, bend, twist). The wearable electronic can distinguish various mechanical stimuli with different directions (Fig. 5a) (Park *et al.*, 2014).

Capacitor-based pressure sensor plays important role in e-skin tactile applications. The change in the distance between the electrodes, inducing the change of the capacitance, is commonly used to measure the external force. The thickness of the elastic materials such as PDMS is easily tunable via external pressing, which is a promising candidate for pressure sensors based on capacitor (Mannsfield *et al.*, 2010). Qiu *et al.* presented a homogeneous 3D hybrid network based on graphene nanoplates/carboxyl-functionalized MWCNTs/silicone rubber composites. The conductive sponge-based capacitive tactile sensor exhibits fast response time (~ 45 ms), low-pressure detection limit (~ 3 Pa), and great sensitivity (~ 0.062 kPa $^{-1}$). The device can be applied in the wearable e-skin for physiological stimuli and micro-pressure monitoring (Fig. 5b) (Qiu *et al.*, 2019).

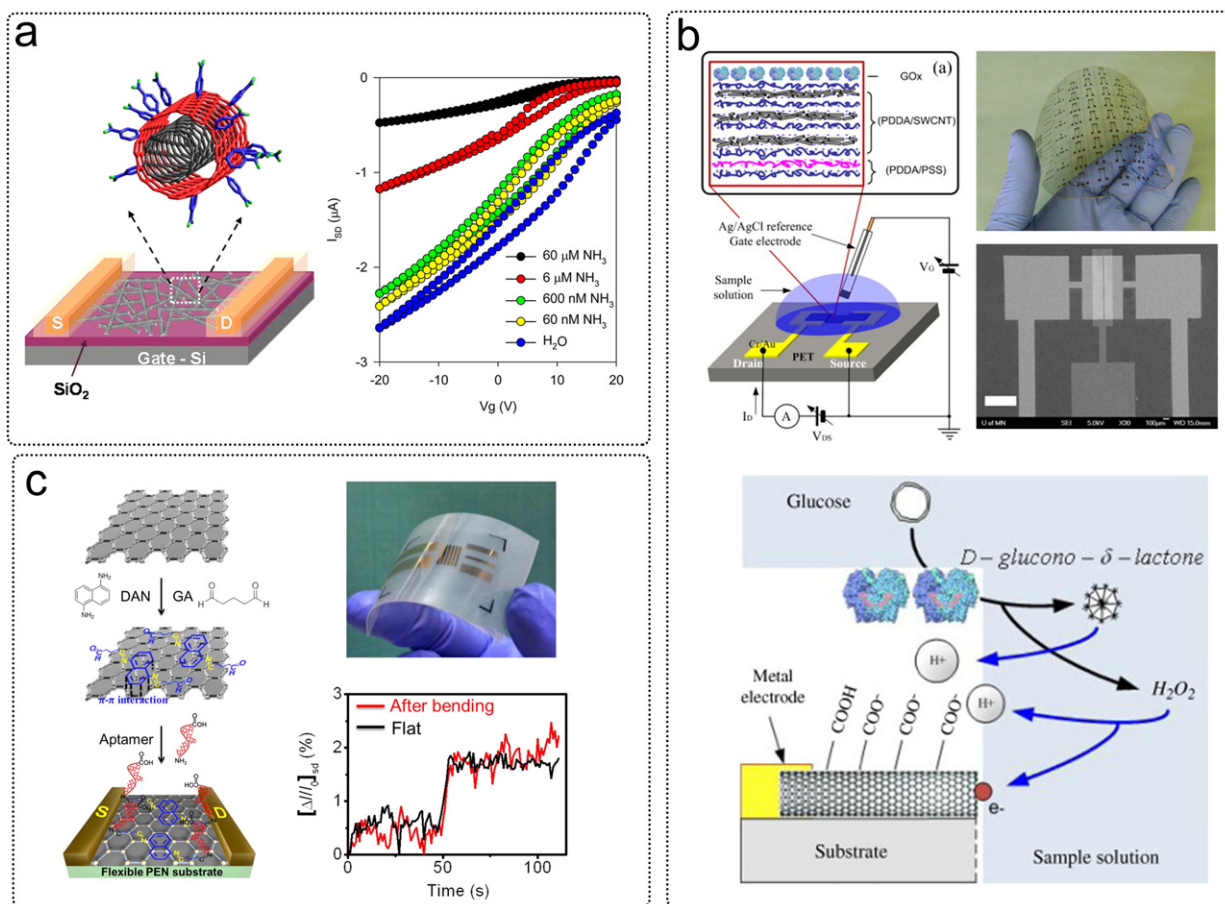


Fig. 6 (a) Schematic diagram of a functionalized-DWCNT TFT platform, transfer curves as a function of NH₃ concentrations. (b) Schematic diagram of the fabricated flexible SWCNT ISFET sensors for pH/glucose sensing, standard 4 in. wafer level devices with a demonstrative bending. (c) The synthetic protocol of flexible graphene-based aptasensor on PEN film, flexible and transparent graphene film deposited the gold electrodes, sensing behavior of the sensor toward 10 pM of Hg²⁺ after 100 cycles of bending/relaxing. Reproduced from Huang, J., Ng, A.L., Piao, Y., *et al.*, 2013. Covalently functionalized double-walled carbon nanotubes combine high sensitivity and selectivity in the electrical detection of small molecules. *J. Am. Chem. Soc.* 135 (6), 2306–2312. Copyright 2013, American Chemical Society. Lee, D., Cui, T., 2010. Low-cost, transparent, and flexible single-walled carbon nanotube nanocomposite based ion-sensitive field-effect transistors for pH/glucose sensing. *Biosens. Bioelectron.* 25 (10), 2259–2264. Copyright 2010, Elsevier Publishing Group. An, J.H., Park, S.J., Kwon, O.S., Bae, J., Jang, J., 2013. High-performance flexible graphene aptasensor for mercury detection in mussels. *ACS Nano* 7 (12), 10563–10571. Copyright 2013, American Chemical Society.

In the other hand, the applied force also can generate a voltage via piezoelectricity function in the novel designed materials or interfaces, which is an effective method to characterize applied force. The external force would cause a change of the dipoles of the materials, generating the compensating charges on the electrodes. This mechanism is essential in the development of the nanogenerator without the requirement of external power supply for practical applications (Chun *et al.*, 2019). PDMS, PET, ferroelectric polymers, carbon-based conductors, and other functional nanocomposites were commonly utilized to fabricate high-performance tactile sensors. Zhao *et al.* designed a fully transparent and highly stretchable triboelectric nanogenerator (TENG) for tactile sensing applications. A double-network ionogel was fabricated as the conductive electrode and one friction layer. The flexible TENG device exhibits a maximum sensitivity of 1.76 V N⁻¹ and maintains a great linearity with various tensile ratios. The promising structure provides the potential for the applications in human-machine interfaces and robotic dexterous manipulations (Fig. 5c) (Zhao *et al.*, 2019).

Chem-/Bio-Sensors

Flexible chemical and biological sensors are also essential for gas detection (e-nose), liquid detection (e-tongue), and healthcare monitoring. The rigid sensing devices based on CNTs, graphene, and organic semiconductors have been reviewed. CNT-based sensor is an important type of sensor. The flexible chemiresistive or FET-based sensors based on CNT as the active layer have been demonstrated for numerous gas analytes or volatile organic compounds (VOCs), including NO₂, NH₃, EtOH, and DMMP (Wang *et al.*, 2020; Saetia *et al.*, 2014). To provide the sensing capability to the specific volatile organic compounds (VOCs) with relatively

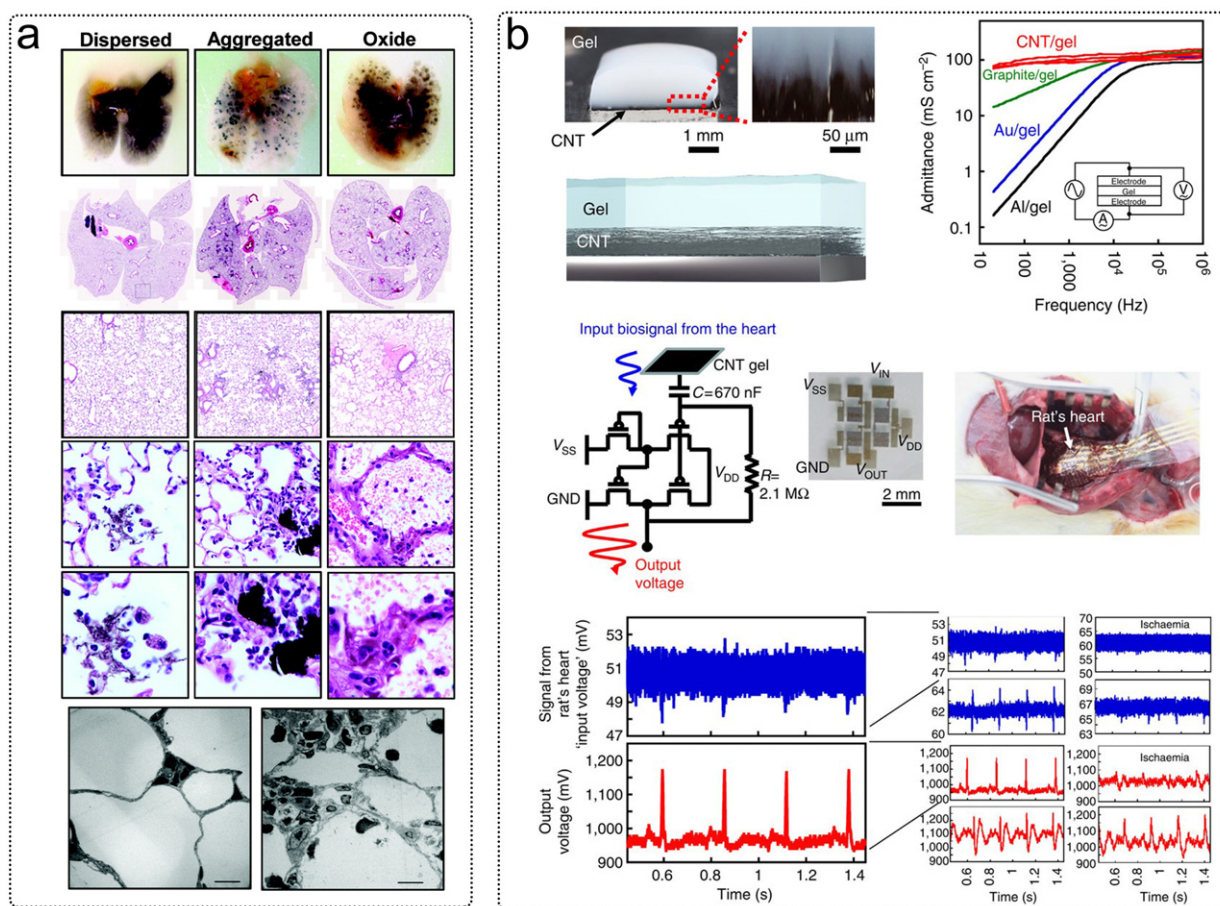


Fig. 7 (a) Graphene oxide induces acute lung injury in mice. Mice were treated intratracheally with three preparations of graphene: highly dispersed and purified in 2% Pluronic (Dispersed, D), aggregates suspended in water (Aggregated, A) or GO (Oxide, O) and the appropriate controls, water (-) or 2% Pluronic (-)P. Twenty-four hours later the mice were sacrificed for assessment of lung injury. (b) Schematic cross-sectional photographs of the conductive gel, electrocardiogram using conductive gel probes and ultra-flexible organic circuit. Reproduced from Duch, M.C., Budinger, G.R.S., Liang, Y.T., *et al.*, 2011. Minimizing oxidation and stable nanoscale dispersion improves the biocompatibility of graphene in the lung. *Nano Lett.* 11 (12), 5201–5207. Copyright 2011, American Chemical Society. Sekitani, T., Yokota, T., Kuribara, K., *et al.*, 2016. Ultraflexible organic amplifier with biocompatible gel electrodes. *Nat. Commun.* 7 (1), 11425. Copyright 2016, Nature Publishing Group.

low chemical inertness, the chemical structure of the CNT was modified with specific functional groups (for example, $\text{-C}_6\text{H}_4\text{COOH}$ for DMMP detection) or treated by various acids and alkalis (Fig. 6a) (Huang *et al.*, 2013).

Moreover, the intrinsic stable CNT-based device can be also applied in liquid phase detection, such as H^+ , glucose, and other biomolecules (Kim *et al.*, 2010; Goh *et al.*, 2018). CNTs can be easily incorporated with specific bioreceptor groups via chemical grafting. With the advantages of fast electron transfer, CNTs can be also applied as electrochemical electrodes for biomolecular detection. For glucose detection, the immobilized glucose oxidase (GOx) can be bonded with the surface of the CNTs. Due to the intrinsic carboxy groups in the chemical structure of CNTs, the conductivity of the CNTs is sensitive to the concentration of H^+ (pH value). Therefore, the CNT-based resistor provides a promising platform for pH and glucose sensing in the further human-body health monitoring (Fig. 6b) (Lee and Cui, 2010).

Graphene is another promising active and electrical transportation material with a low-dimensional structure, high surface-to-volume ratio, and large detection area (Gao *et al.*, 2020; Wang *et al.*, 2016). Similarly, the graphene-based devices exhibit the capabilities of molecular detection. For the practical e-skin applications, the sensing selectivity of device should be improved. Similarly, the graphene-based electronics can be utilized in the liquid-based measurements. Chitosan-glucose oxidase is the most common receptor for glucose detection, which has been widely used in the graphene-based glucose sensors. Graphene has also been modified with DNA chain for targeted RNA recognition. An *et al.* demonstrated a flexible graphene-based sensor with ultrahigh sensitivity, based on modified graphene with aptamer. The active layer was deposited onto a PEN substrate for the fabrication of a flexible sensor, which exhibits an ultrahigh sensitivity for the detection of Hg^{2+} with an ultralow concentration of 10 pM and maintains the operation stability under bending conditions (Fig. 6c) (An *et al.*, 2013).

Organic semiconductors (OSCs) and conducting polymers (CPs) are highly attractive materials with the advantages of low-temperature solution processability, large-area compatibility, and low fabrication cost. The detailed performances of the OSCs and

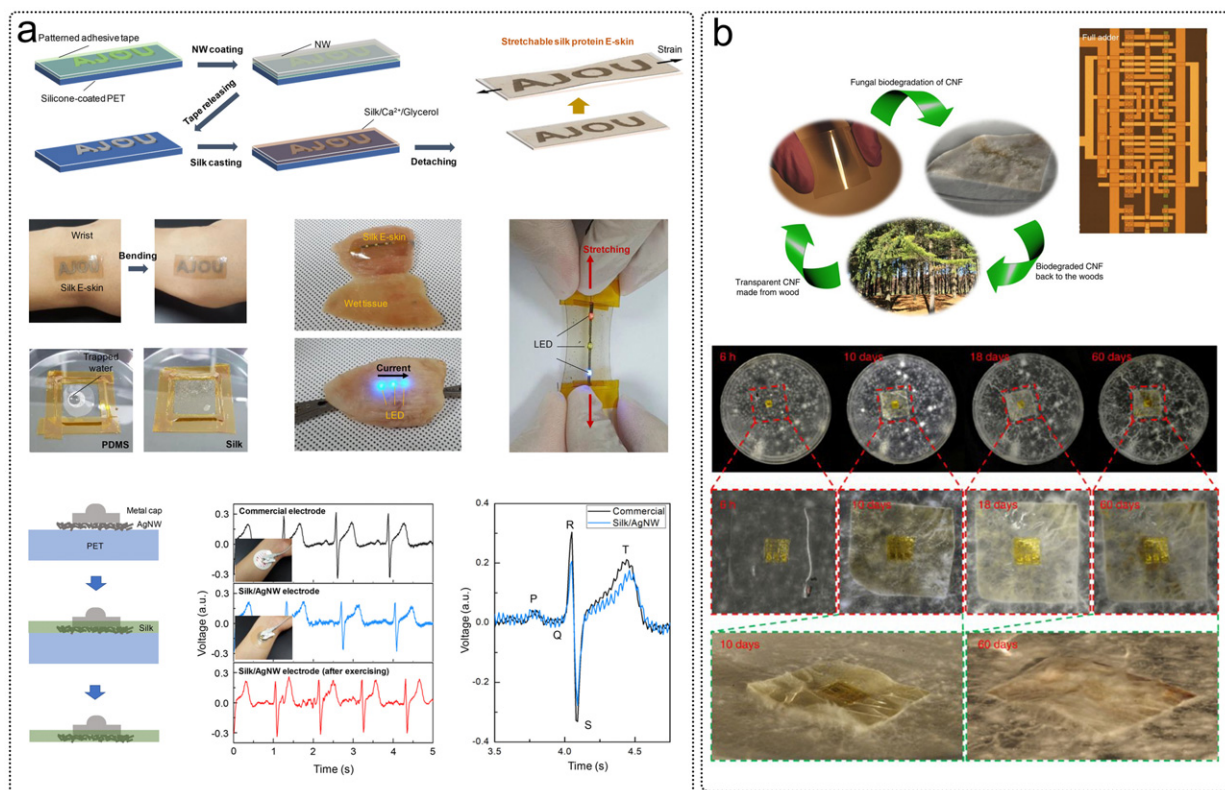


Fig. 8 (a) Skin-adhering, stretchable, conforming silk protein-based hydrogel e-skin, wearable Ag NW/silk electrodes for electrocardiograms (ECGs). (b) Illustration of a likely life cycle of the biobased and biodegradable CNF paper, optical microscopy image of a full adder, fungal biodegradation tests of the CNF-based electronics. Reproduced from Jo, M., Min, K., Roy, B., *et al.*, 2018. Protein-based electronic skin akin to biological tissues. *ACS Nano* 12 (6), 5637–5645. Copyright 2018, American Chemical Society. Jung, Y.H., Chang, T.-H., Zhang, H., *et al.*, 2015. High-performance green flexible electronics based on biodegradable cellulose nanofibril paper. *Nat. Commun.* 6 (1), 7170. Copyright 2015, Nature Publishing Group.

CPs as the active layers can be controlled through the variation of the deposition conditions. For the e-skin applications, the high- k and the ultrathin dielectric is essential to limit the operating voltages (Liao *et al.*, 2015a). Liao *et al.* presented a highly selective organic electrochemical transistor (OECT)-based sensor for H_2O_2 detection via the modification of the gate electrode with a bilayer film (UOX-GO/PANI/Nafion-graphene/Pt gate), which can effectively block the interference from the charged biomolecules and exhibits highly sensitive H_2O_2 detection (Liao *et al.*, 2015b).

Additional Properties

The basic property of the e-skin is to sense the tactile forces with the incorporation of the chemical and biological sensing capabilities. For the practical applications in human life, the biocompatibility is an essential consideration for e-skin devices. The rGO exhibits the better biocompatibility than CNTs with cells (Yun *et al.*, 2017; Takahashi *et al.*, 2017; Lanzani, 2014). For the facilitation of the use of graphene-based materials in widespread applications, Duch *et al.* designed the strategies to improve the biocompatibility of graphene materials in the lung. The biocompatibilities of the aggregated graphene, pluronic dispersed graphene, and graphene oxide (GO) were compared, demonstrating that the toxicity is mainly from the covalent oxidation of graphene, and dispersion of pristine graphene in Pluronic is a candidate for safe biomedical applications (Fig. 7a) (Duch *et al.*, 2011). For organic materials, the chemical composition, the solvent, the surface charge, and the pH would affect the cytotoxicity. Several polymers are exhibiting a certain degree of biocompatibility. Sekitani *et al.* demonstrated a biocompatible conductive gel. On implantation into a living tissue for 4 weeks, it shows a small foreign-body reaction, compared with the metal-based device (Fig. 7b) (Sakitani *et al.*, 2016).

Using natural materials is another promising route to improve the biocompatibility of the flexible electronics, such as starches, celluloses, and chitins, which have been demonstrated as substrates for flexible electronics. Jo *et al.* designed a composite based on a metallic nanowire network and silk protein hydrogel for skin-adhering e-skin. This membrane provides a channel as interface with vital bio-signals from the tissues (Fig. 8a) (Jo *et al.*, 2018). Resorbable and degradable substrates can also play an important role in the e-skin on the human body. Jung *et al.* purposed a flexible microwave and digital electronic on cellulose nanofibril paper and the successful fabrication of key electrical components with biodegradability (Fig. 8b) (Jung *et al.*, 2015).

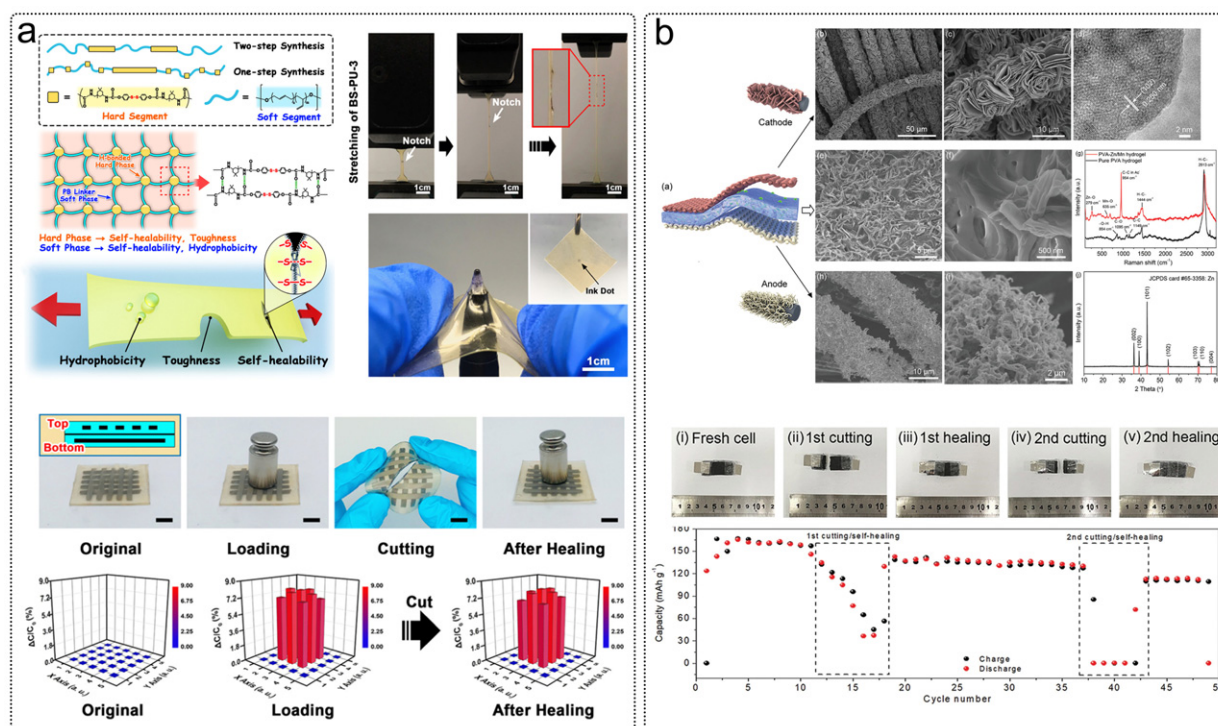


Fig. 9 (a) Molecular and schematic designs, a notched BS-PU-3 specimen and puncture demonstration, schematic illustration and optical images of pressure-sensing array detecting a weight before and after self-healing. (b) Illustration of the self-healing flexible Zn-ion battery, photo of the battery after cutting and healing and the corresponding cycling performance. Reproduced from Ying, W.B., Yu, Z., Kim, D.H., *et al.*, 2020. Waterproof, highly tough, and fast self-healing polyurethane for durable electronic skin. *ACS Appl. Mater. Int.* 12 (9), 11072–11083. Copyright 2020, American Chemical Society. Liu, J., Long, J., Shen, Z., *et al.*, 2021. A self-healing flexible quasi-solid zinc-ion battery using all-in-one electrodes. *Adv. Sci.* 8 (8), 2004689. Copyright 2021, Wiley-VCH.

The bio-skin has the ability to repair the damaged surface. For the artificial e-skin, the damage repairing ability is an advantage in the practical applications. To add the self-healing functions in electronics, developing the hybrid materials with healing components or novel chemical structure with reversible bonds in the materials is the promising strategy for the fabrication of the self-healing electronics (Fig. 9a) (Tong *et al.*, 2021; Kang *et al.*, 2019; Ying *et al.*, 2020). Liu *et al.* reported a self-healing flexible Zn-ion battery consisting of the all-in-one cathode (VS₂ nanosheets on carbon materials) and anode (electrochemical-deposited Zn nanowires). The battery maintains high potential after healing from cutting into six pieces with the operation stability under various bending conditions. The temperature sensing properties is important in human skin, which helps to collect the environmental information and prevent the burn injury. For the requirement of the portability and long-time operation properties, many technologies have been developed for power generation and storage in the flexible and e-skin electronics (Fig. 9b) (Liu *et al.*, 2021).

Highly-Integrated e-Skin

E-skin is an electronic system that integrates various high-performance sensors on a flexible substrate. It can simulate human skin to sense the subtle stimulus signals from the outside world. Similar to human skin, e-skin also has ductility and mechanical durability as well as the ability to sense temperature and pressure. In recent years, the sensors in the e-skin have been transformed from single-mode to multi-functional, and the sensing effects include pressure, temperature, and humidity. The integrated e-skin is getting closer to the real skin (Chortos *et al.*, 2016).

Motion sensing is one of the most important technologies in artificial intelligence. The development of motion sensing function in e-skin is usually to integrate the pressure sensor unit into the digital array. With the development of highly integrated e-skin, the research of self-powered e-skin is favoured by researchers. It provides the feasibility for the development of the portable electronic system and is a promising next-generation intelligent and interactive product. Guo *et al.* reported a multi-functional e-skin, which can be self powered and integrate the detection of physical information such as speed, acceleration, motion tracking and pressure. This kind of self-power e-skin has a wide application prospect (Guo *et al.*, 2020).

Self-power feature is an essential function in the implantation of e-skin for healthcare. Yu *et al.* prepared a kind of Nano Engineering flexible electrochemical patch by using bio fuel cell (BFC) array and biosensor array for energy collection and molecular analysis of human sweat. The flexible patch is then integrated on ultra-thin polyimide (PI) substrates via flexible interconnects for power management, signal processing and wireless transmission. Then a flexible, fully integrated, self-powered

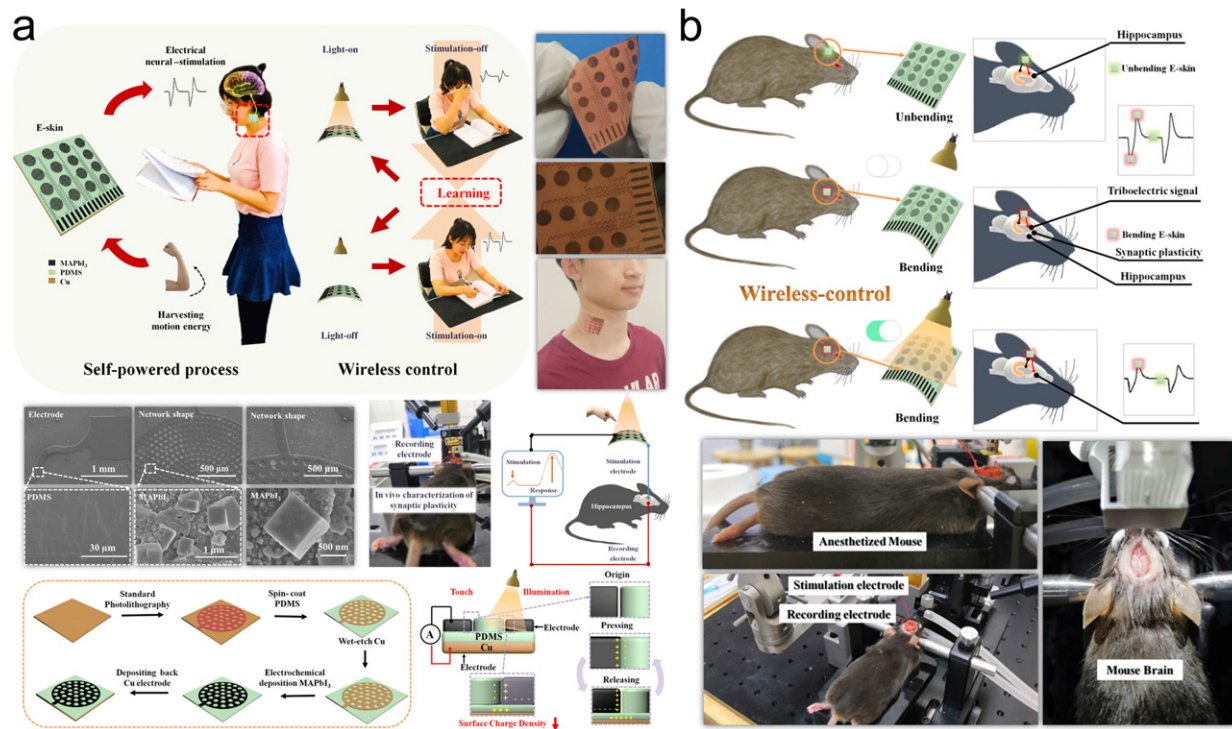


Fig. 10 (a) Experimental design, device structure, material system, animal experiment, fabrication process and working mechanism of the e-skin. (b) The e-skin linking to mouse brain for synaptic characterization in hippocampus. Reproduced from Guan, H., Lv, D., Zhong, T., *et al.*, 2020. Self-powered, wireless-control, neural-stimulating electronic skin for in vivo characterization of synaptic plasticity. *Nano Energy* 67, 104182. Copyright 2020, Elsevier Publishing Group.

e-skin platform was developed, which can provide real-time, continuous, multi-channel sensing, and wireless transmission of data to the user interface through Bluetooth communication. The development of this technology enriches the functions of e-skin and has broad application prospects in the fields of robotics and wearable health care (Yu *et al.*, 2020).

For the data collection, wireless communication will promote the development of the portable device and e-skin. Guan *et al.* developed flexible photosensitive-triboelectric units using MAPbI₃/PDMS to make e-skin. The electrical nerve-stimulation signal of e-skin is generated by human activities without an external power supply. This kind of neural modulation can be regulated by the intensity and wavelength of light signal. Furthermore, the researchers connected the device to the hippocampus of mouse brain, proving that e-skin can generate electrical stimulation to stimulate brain activity and induce postsynaptic response, which can be used to characterize synaptic plasticity in vivo. This kind of self-powered photo-operate e-skin has important research significance in wireless-control, battery-free and electrical nerve stimulation systems, and also has potential application value in biomedical engineering and neuroscience (Fig. 10) (Guan *et al.*, 2020).

The human skin has multi function such as temperature sensing, pain perception, and pressure sensing. Hua *et al.* fabricated a highly stretchable and conformable matrix network (SCMN), inspired by the skin, which has successfully expanded the e-skin sensing function. As a multi-sensory e-skin, it can simultaneously detect temperature, strain, humidity, light, magnetic and pressure, and has adjustable sensing range and large area scalability, which may be suitable for high-density 3D integrated solutions. Furthermore, the researchers have built a personalized intelligent prosthesis, which can not only get the pressure distribution on the finger, but also estimate the temperature of the grasping object at the same time. This new type of e-skin has shown great application potential in humanoid robot, new prosthesis, human-machine interface and health-monitoring technology (Fig. 11) (Hua *et al.*, 2018). Zhu *et al.* designed a e-skin based on coaxial piezoelectric fiber, which was constructed with three layers of flexible and stretchable materials. An elastic polyurethane (PU) film was utilized as the supporting substrate and the novel coaxial flexible piezoelectric nanofibers (NFS) fabricated by electrospinning technology were used as the core sensing layer. High piezoelectric inorganic barium titanate (BTO) nanoparticles (NPs) and polarized organic polyvinylidene fluoride (PVDF) polymers doped with graphene oxide (GO) nanosheets are introduced, the synergistic effect of these materials improves the piezoelectric properties of nanofibers. Due to the synergistic effect of coaxial structure, the e-skin with high shape adaptive characteristics has good sensing performance and excellent mechanical durability. In addition, it can detect and quantify all kinds of human motion related to joints. It can also be integrated into the pressure sensing matrix, which can distinguish different shapes of objects for real-time tactile mapping. The development of this kind of e-skin has great application significance in the development of advanced medical monitoring electronic products, the next generation of intelligent robots and the next generation of prosthetics (Zhu *et al.*, 2020).

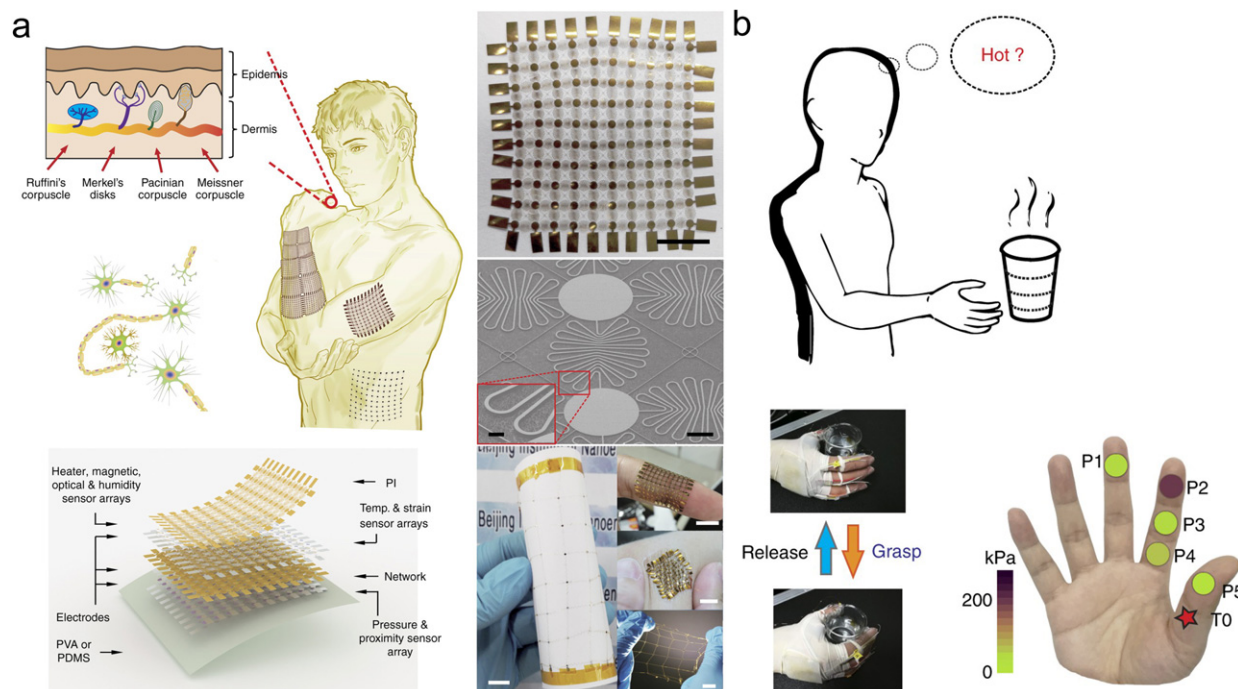


Fig. 11 (a) Skin-inspired highly stretchable and conformable matrix network, (b) The intelligent prosthetic hand with personalized SCMN configuration. Reproduced from Hua, Q., Sun, J., Liu, H., *et al.*, 2018. Skin-inspired highly stretchable and conformable matrix networks for multifunctional sensing. *Nat. Commun.* 9 (1), 244. Copyright 2019, Nature Publishing Group.

Summary and Outlook

In this article, we reviewed the recent researches in flexible electronics, starting from the key flexible materials including conductors, semiconductors, and substrates. The functional flexible electronics were reviewed including the tactile sensors, bio-/chemi-sensors, and power-supply devices. Many efforts have been done on the design of unique flexible structures. For the final goal of the flexible devices, stretchability has been purposed to promotes the process to practical applications of flexible electronics, together with the essential features such as biocompatibility, self-power, and self-healing capability.

At present, scientists have developed advanced materials and structures with flexibility and stretchability inspired from the natural biomass and the nanostructures of human skin, which have been applied in high-performance sensors, batteries, and solar cells. Many works mainly focus on the single function of one device. It is still a challenge of the integration of the many kinds of devices into one electronic system, because of the different key materials and nanostructures in different devices. For the practical applications in wearable e-skin and the implantable electronics in the human body, new requirements and limitations were purposed including wireless communications, biocompatibility, biosafe, biodegradability, self-power, and self-healing, which put forward a new challenge to develop a highly-integrated biosafe, durable, self-power electronic system for practical applications. The device functions and structures were well studied and investigated in the previous reports. Future researches should further design the strategy to integrate the current function devices and evaluate the biosafe from chemical structure and materials to device and equipment manufacturing.

Current sensing systems are mainly operated with an external power supply, while the TENG can work as self-power sensors. However, the TENG could only detect mechanical forces. New self-power sensor should be developed to detect other mechanical and chemical signals. Synaptic devices and neuromorphic computations are highly attractive fields in signal processing systems and artificial neural networks. Incorporation with synaptic functions would provide the self-processing capabilities and the performances of the artificial e-skins.

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Organic Neuromorphic Systems

Bosheng Zhou and Jia Sun, Hunan Key Laboratory for Super Microstructure and Ultrafast Process, School of Physics and Electronics, Central South University, Changsha, Hunan, PR China and Hunan Key Laboratory of Nanophotonics and Devices, School of Physics and Electronics, Central South University, Changsha, Hunan, PR China

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Abstract

Organic neuromorphic system (ONS) is the bridge between building organic devices and the biological nervous system. Because organic neuromorphic devices (ONDs) have the excellent flexibility, low power consumption and biocompatibility, it can be predicted that this field will be a very promising direction for future development. Firstly, this chapter introduces the synaptic functions of ONDs. Next, we introduce five different working mechanisms of two-terminal ONDs and four different structures of three-terminal ONDs. Then, we describe how individual devices can be composed of multiple-input and multiple-output structures, which are of great significance for modeling the structure of nerve cells. Finally, we conclude the application of ONDs in intellisense, neuromorphic chip and flexible e-skin, and provide a summary and outlook for the development of ONS.

Key Points

- Analyzes the working mechanisms of various two-terminal and three-terminal organic neuromorphic devices.
- Presents how organic neuromorphic devices can be composed of multiple-input and multiple-output structures to form the device array.
- Introduces the latest applications of organic neuromorphic devices in intellisense, neuromorphic chip and flexible e-skin.

Introduction

Neuroelectronics is a newly emerging interdisciplinary field of biology and physics, which mainly studies the simulation of signal transmission between neurons by electronic devices. Neuromorphic system is a prime example of that (Tuchman *et al.*, 2020). In the mid-20th century, scientists have created the devices similar to artificial synapses by complementary metal-oxide-semiconductor (CMOS) technology, (Hosticka, 1998) but the early “artificial synapse” was too energy-intensive for high-density integration. Until 1980s, the research on the neuromorphic functions of electronic devices has entered a golden age. Compared to traditional electronic devices, organic neuromorphic devices (ONDs) cleverly incorporate the concept of bionics, which allows devices to be smaller and transmit information efficiently by mimicking biological neural synapses. In addition, because the device uses organic materials, it has better biocompatibility and flexibility, and also makes it cheaper to prepare. These advantages make OND have a wide application prospect in intellisense, flexible and wearable electronics, biomedicine and so on.

The OND is an important unit of organic neuromorphic system (ONS). Depending on the structure of devices, OND can be simply divided into the memristor based two-terminal (2T) structure and the transistor based three-terminal (3T) structure. For ONDs, the ‘organic’ primarily refers to the organic semiconductor (OSC) active layer, which is the core of OND. Although inorganic materials have made progress in neural devices, (Fu *et al.*, 2018a) OSC has attracted more interest due to their intrinsic advantages as mentioned above (Gumyusenge *et al.*, 2021). According to the classification of organic matter, OSC materials include organic polymers (such as Poly (3,4-ethylenedioxythiophene) (PEDOT), Poly (3-hexylthiophene) (P3HT) (Rivnay *et al.*, 2016; Qian *et al.*, 2016) and organic small molecules (such as 2,7-Dioctyl (Tuchman *et al.*, 2020) benzo[thieno[3,2-b] (Tuchman *et al.*, 2020) benzo[thio-phenene (C8-BTBT), (Haase *et al.*, 2018) pentacene, (Alibart *et al.*, 2010) etc.). In addition, OSC can be doped to improve device performance, such as PSS in PEDOT and metal particles in pentacene (Alibart *et al.*, 2010). Meanwhile, organic heterojunction structures with different electrical conductivity have been widely studied recently (Qian *et al.*, 2017a; Qiao *et al.*, 2015).

In this chapter, we first introduce the biological synaptic functions of OND, and then we mainly discuss the working principles of 2T and 3T devices. Finally, we present the prospect of applications of these periods in ONS, such as intellisense, neuromorphic chip and flexible e-skin.

Synaptic Functions

The human brain has tens of billions of nerve cells, each of which can communicate with its neighbors through synapses, forming a complex biological neural network. Fig. 1a shows the structure of nerve cells and synapse. Take an example of the visual

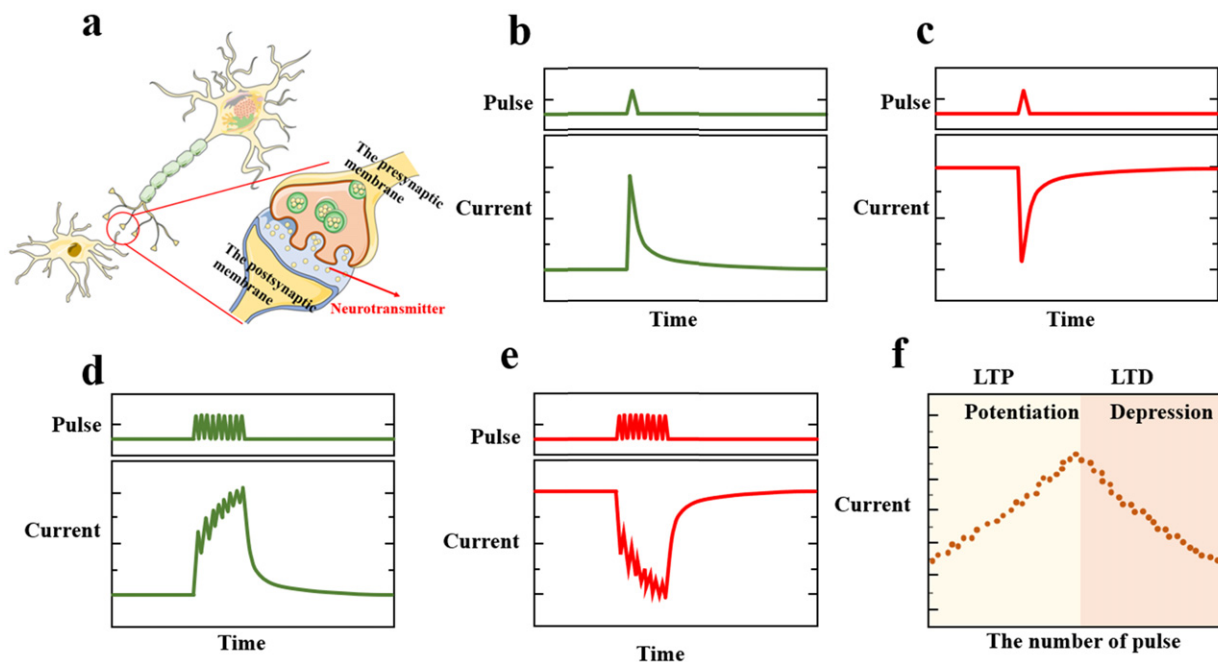


Fig. 1 (a) The structure of synapse. (b–e) Relaxation properties of synapses. The green line is EPSC, and the red line is IPSC. (f) The number of pulses can cause the change in synaptic function.

formation, retinal cells feel light stimulation and produce electrical signal firstly, then the signal transmission to the synapses, stimulates the presynaptic membrane release neurotransmitters. Next, neurotransmitters are picked up by the postsynaptic membrane and reconstitute electrical signals. Finally, the signals travel to the brain and form vision.

ONDs can realize signal transformation and transmission by simulating biological synapses, and simultaneously show certain biological synaptic functions (Wan *et al.*, 2020). The input end of the ONDs mimics the presynaptic membrane, and the output end mimics the postsynaptic membrane. Specifically, synaptic function refers to the memory properties of signals transmitted through the synapse. Due to delayed transmission of neurotransmitters in the synaptic cleft, signals in the postsynaptic membrane will relax after input from the presynaptic membrane. The synaptic response time is usually at the magnitude of millisecond. Figs. 1b and c well reflect the relaxation characteristics of synapses, in which the former is excitatory postsynaptic current (EPSC) and the latter is inhibitory postsynaptic current (IPSC). When the presynaptic membrane applies an electrical pulse, the current in the postsynaptic membrane peaks momentarily and then declines slowly. If continuous electrical pulses were applied to the presynaptic membrane, EPSC would show an upward trend until reaching the peak value, as shown in Fig. 1d. After the removal of electrical pulses, EPSC would slowly decrease to the initial value. The corresponding IPSC presents the opposite characteristics of EPSC, as shown in Fig. 1e (Sun *et al.*, 2018). Repeated electrical stimulation can lead to increased neuron weight and the formation of new synapses, (Lamprecht and LeDoux, 2004; Chang *et al.*, 2011) which may be related to short-term plasticity and long-term plasticity, respectively. In addition, studies have shown that the synaptic function of OND is related to many factors, such as pulse intensity and pulse duration. For example, as shown in Fig. 1f, the function of the device may change from long-term potentiation (LTP) to long-term depression (LTD) by changing the pulse conditions. Meanwhile, synaptic functions of ONDs also include spike-timing-dependent plasticity (STDP) and spike-rate-dependent plasticity (SRDP) (Abbott and Nelson, 2000). The synaptic function of OND is one of the important indicators to measure the device performance, which is closely related to the material, preparation process and device structure (Wan *et al.*, 2019).

2T ONDs

The 2T structure in ONDs is the simplest structure for input-interlayer-output similar to sandwich structure. The basic principle is that the signal applied at the input will cause the resistance of the active layer to change, so that the signal at the output will be modulated. Simultaneously, in order to perform synaptic function, the active layer must have carrier storage capability, which is similar to the relaxation properties for neurotransmitter transmission in synaptic cleft. Usually, 2T devices have simple structure and easy preparation, and easy to integrate in large and dense crossbar arrays (van De Burgt *et al.*, 2018). According to the different resistance change modes of the active layer, the principle of 2T devices can be divided into redox reaction, charge trapping, ion migration, metal filament conducting and photocarriers.

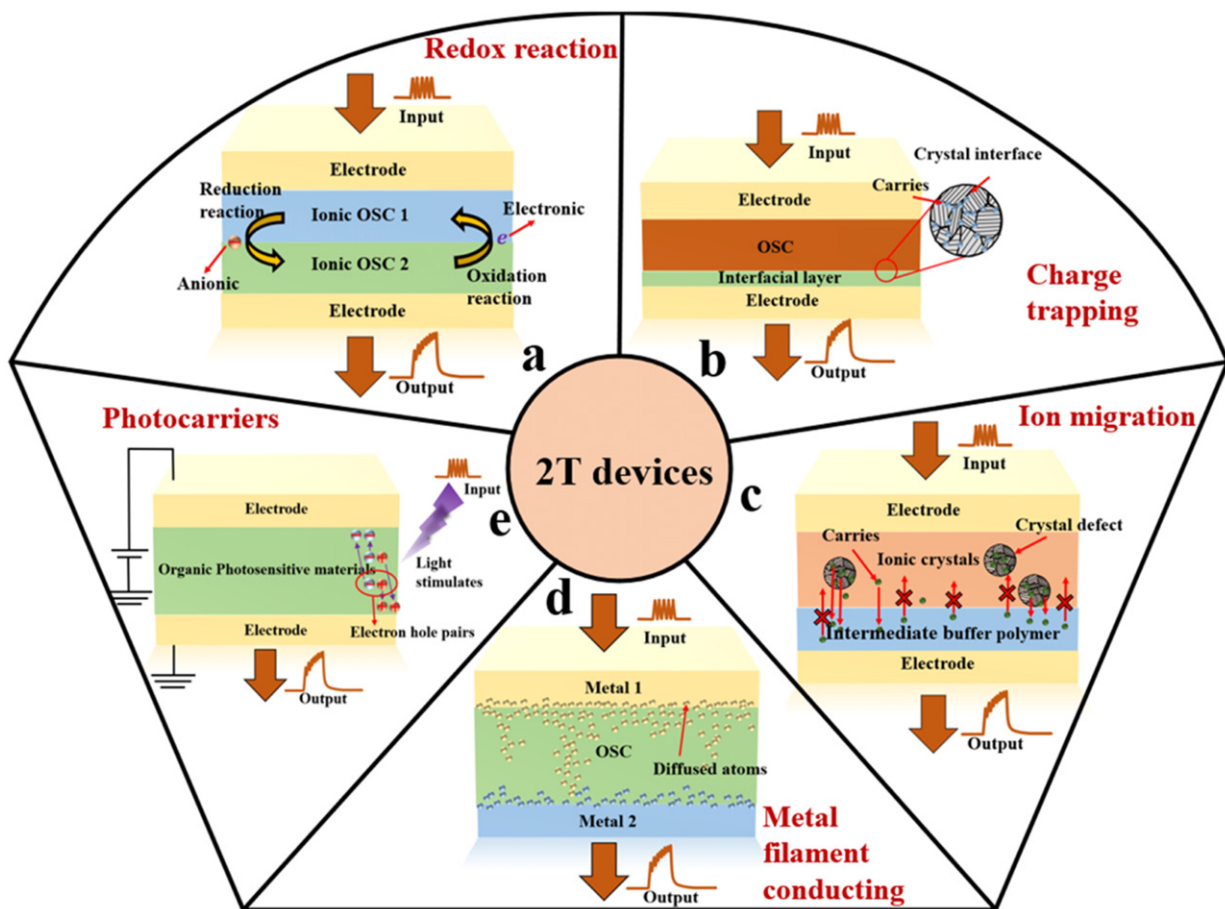


Fig. 2 The working principles of five types of 2T devices.

Redox Reaction

Chemical redox reactions are associated with the movement of ions and the transfer of electrons. Due to the time required for chemical reactions and the relaxation of ions across interfaces, and the resistivity is different before and after the reaction, synaptic functions can be realized based on this principle. As shown in Fig. 2a, we assume that reduction reaction takes place in ionic OSC 1, then the reduction product anions can enter ionic OSC 2 under the action of electric pulse, where the oxidation reaction takes place. To balance the charge, the electrons or oxidation products lost in the oxidation reaction are recycled into the ionic OSC 1. Until the disappearance of electric pulse, due to the presence of chemical reaction and ion migration there is a certain relaxation, so that the output current has memory characteristics, showing synaptic function (Liu *et al.*, 2016). However, some redox reactions are accompanied by a large amount of heat release, which may lead to device instability, so its application prospects are greatly limited.

Charge Trapping

Charge trapping makes use of the adsorption capacity of crystal defects on carriers, which can cause relaxation of carriers' movement, as shown in Fig. 2b. There are many crystal defects at the interface layer, such as grain boundaries, vacancies, and dislocations, which can bind carriers for a period of time. The OSC layer is a non-intrinsic semiconductor material with many carriers. When the electric pulse is applied, the carriers migrate to the interface layer and are captured by the crystal defect. After the removal of the electric pulse, the carriers can still be stored for a period of time and then released slowly, making the device show the memory function. This is also the principle of the most common 2T devices. For example, Ji *et al.* inserted the multilayer graphene into the polyimide layer and obtained a memristive device with high ON/OFF ratio (Ji *et al.*, 2012).

Ion Migration

The ion migration takes advantage of the binding properties of buffering polymers to ions. As shown in Fig. 2c, the active layer consists of ionic crystal and intermediate buffer polymer. Different from the charge trapping that defect only exist at the interface, there are also a lot of crystal defects inside the ionic crystal, which can generate many anions and cations. When the pulse is

applied, some ions in the ion crystal are repelled into the intermediate buffer polymer layer. But when the pulse is removed, the ions in the buffer polymer will be strongly bound and difficult to return to the ion crystal, resulting in memory. When the electrical pulse is very weak, the ion doesn't have enough kinetic energy to break through the interface and into the buffer polymer, so some noise signals can be excluded. The filtering function of ion migration may be used in the information processing of the brain, so that electrical signals above characteristic intensity can be output. Take an example of memristive device by Xu *et al.* they use the perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ as ionic crystal and BCCP (a hybrid polymer) as a buffer polymer, simulated a variety of synapse functions (Xu *et al.*, 2016).

Metal Filament Conducting

Metal filament conducting makes use of the diffusion of metal atoms to cause the change of resistivity. As shown in Fig. 2d, metal 1 is easily diffused by external electric field, while metal 2 has a low diffusion coefficient. After the pulse was applied, the atoms at the metal 1 interface quickly sense the same charge and repelled each other, resulting in an increase in the diffusion coefficient. Because the OSC layer is very thin, the effect of metal atom diffusion is obvious. The farther the diffusion distance, the lower the resistivity of the device (Li *et al.*, 2013; Zeng *et al.*, 2014). When the outer field is removed, the atoms gradually return to the interface due to adsorption, but this process takes a long time, indicating that the devices based on metal filament conducting have a good memory effect. But if the opposite voltage is applied, the atoms in OSC will quickly come back to the interface and make memory erased.

Photocarriers

Unlike the other types described above, 2T ONDs based on photocarriers use the optical pulses as an input. As shown in Fig. 2e, the photosensitive OSC material in the middle is irradiated by light pulse, exciting the photosensitive material to produce electron hole pairs. When a fixed voltage is applied to the electrodes at both ends, the electron-hole pairs will separate and move to the boundary of the photosensitive material, which changes the conductivity of the device. Due to the existence of shallow impurity levels as traps in OSC, the recombination of non-equilibrium carriers has a long relaxation, which causes the output current with memristive feature (Xue *et al.*, 2020). Under different illumination, the device can switch between high and low resistance states, and simple optical switch can be realized.

3T ONDs

Since the invention of transistor in 1947, the research of electronic devices has entered a period of rapid development (Bardeen and Brattain, 1948). Especially for the proposed concept of 3T structure of the field effect transistor (FET), it plays a huge role in promoting the development of electronic industry. The structure of 3T ONDs is based on the source, drain and gate structure of the FET. Through inputting signals in the gate, after a series of processing, then output in the form of source drain current, which can realize the integration and amplification of the signal. In recent years, 3T ONDs have also been introduced into the field of ONS. 3T ONDs are functionally similar to 2T ONDs, but the former has attracted increasing interest in recent years because 3T ONDs allow more flexible control of carrier transport by controlling the gate, and 3T ONDs are compatible with CMOS technology. According to the gate position, the structure of 3T OND is divided into top-gate structure and bottom-gate structure. There is no significant difference between them in device performance, so the schematic diagram in this chapter is presented in the form of bottom-gate.

The organic field-effect transistor (OFET) is one of the most common and simplest 3T ONDs, which is the prototype of other 3T ONDs. The principle of OFET is applying a constant voltage between the source and drain, while voltage signals are applied in the gate, which creates charges at the interface between the dielectric layer and the OSC layer, then lead to the change of channel resistance and affecting the source and drain current (Nikolka *et al.*, 2017). We define the partial derivative of the I_D with V_G as the transconductance (G_m) of the device:

$$G_m = \frac{\partial I_D}{\partial V_G} \quad (1)$$

The transient G_m of OFET can be described by the following formula:

$$G_m = \frac{W}{L} \cdot \mu \cdot C' \cdot (V_{th} - V_G) \quad (2)$$

Where L and W represent channel length and width respectively, μ is carrier mobility, C' is capacitance per unit area, and V_{th} is the threshold voltage. The G_m and response time of 3T ONDs are the key factors to determine their performance. For OFETs, there is almost no time relaxation between the gate voltage input and the induced charge generated at the interface, so OFETs are not suitable as memristive synaptic devices. However, many new devices have emerged based on OFET structures, among which the following examples are typical.

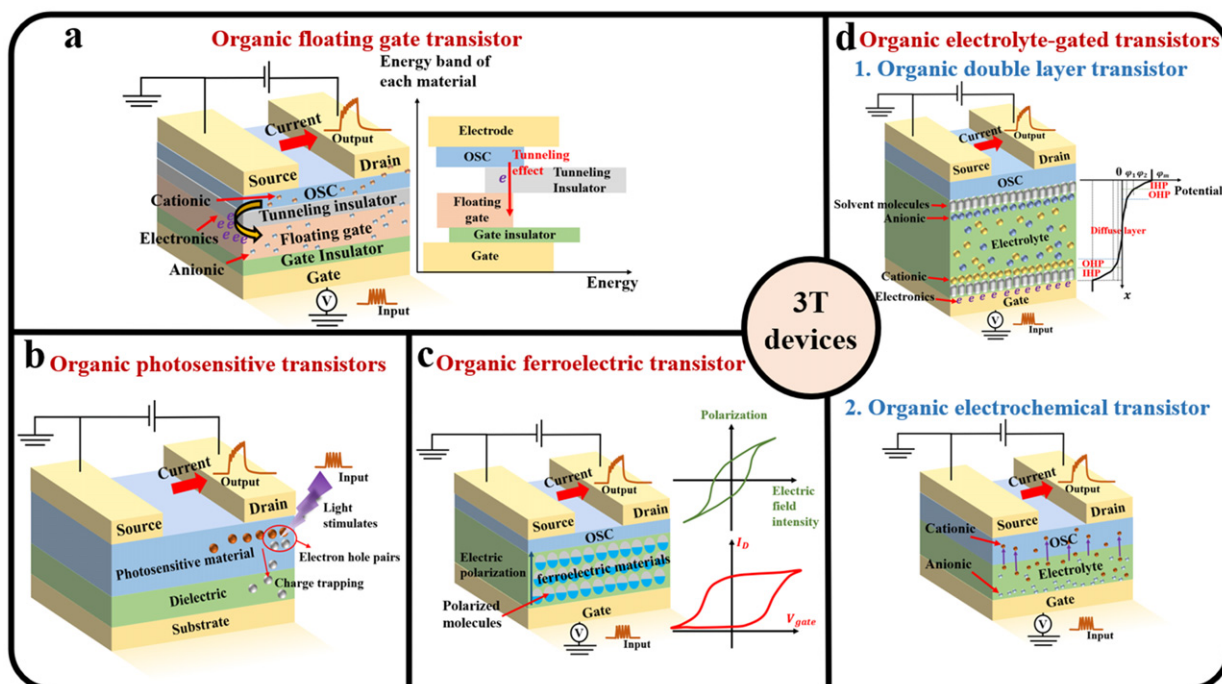


Fig. 3 The working principles of five types of 3T ONDs.

Organic floating gate transistor

Organic floating gate transistor (OFGT) makes use of the quantum tunneling effect to capture the carrier, thus realizing the memory effect. In **Fig. 3a**, the structure diagram of the device is on the left, and the band diagram of each layer is on the right. When positive gate pressure is applied, the electrons in OSC can pass through the insulating layer with high barrier and enter the floating gate through tunneling effect. However, when the gate voltage is removed, the electrons cannot tunnel back to OSC again because the floating gate layer is clamped by the insulating layer with high potential barriers at both ends. In addition, when negative gate pressure is applied, the electrons in the floating gate can be released, so as to achieve memory erasure (Van Tho *et al.*, 2016; Fuller *et al.*, 2019). Tunneling of electrons follows quantum laws, which provides a basis for quantitative analysis of device properties.

Organic Photosensitive Transistor

Organic photosensitive transistor (OPT) is a 3T structure based on photocarriers, which is functionally similar to 2T ONDs introduced in Section “Photocarriers”, both of which convert light pulses into synaptic currents. As shown in **Fig. 3b**, photosensitive materials can both generate electron hole pairs by illumination and act as channels. Because there are many crystal defects on the interface between dielectric and photosensitive layer, when the electron hole pair is generated, it will capture a class of carriers. While the illumination stops, the trapped carries by dielectric will be released. Therefore, the source-drain current produces a memristive effect (Mao *et al.*, 2019). Because the difference of light intensity and frequency can change source-drain current, the researchers have realized the logical input of optical signal by designing optical multi-inputs. In addition, OPT has been widely applied in ONS, such as image recognition, optical sensing and so on.

Organic Ferroelectric Transistor

The relationship between the polarization intensity of ferroelectric materials and the change of electric field has memory characteristics, as shown in the green line in **Fig. 3c**, which is called the hysteresis loop. Many studies indicate that the formation of the hysteresis loop may be related to the polarization inversion of material molecules. Using this characteristic of ferroelectric materials, the synaptic function of 3T ONDs can be realized (Zhong *et al.*, 2020; Pei *et al.*, 2021). As shown in the **Fig. 3c**, the electric field intensity at the interface between ferroelectric material and OSC will directly affect the carrier mobility in the channel, leading to the change of source-drain current. With the change of gate voltage, the total electric field at the interface will also show memory characteristics (red line in **Fig. 3c**), which has the same trend as the polarization strength of ferroelectric materials.

Therefore, the source-drain current can show the memory (Tian *et al.*, 2019). Because the hysteresis loop of ferroelectric material has almost perfect centrosymmetry, its memory characteristic is also very remarkable.

Organic Electrolyte-gate Transistor

Depending on the electrolyte state, the organic electrolyte-gate transistor (OEGT) can also be divided into organic electric double layer transistor (OEDLT) and organic electrochemical transistor (OECT) (Gerasimov *et al.*, 2019).

Organic electric double layer transistor

OEDLT generally uses ionic solution as electrolyte. For this type of device, the ions in solution generally cannot enter the OSC channel, but due to the special properties of solution, the electric double layer (EDL) structure can be formed, which greatly improves the capacitance of the device (Schmickler, 1996; Desbief *et al.*, 2016). According to the Helmholtz model of EDL theory if a negative voltage is applied at the gate, the EDL structure will be formed as shown in the top of Fig. 3d. The first layer close to the interface is a solvent molecule, called Inner Helmholtz Plane (IHP), followed by a layer of ions with opposite electrical properties to the solid layer on the other side of the interface, called Outer Helmholtz Plane (OHP). The area further away from the interface afterward is called the diffuse layer. Meanwhile, the electric potential varies with the distance from the interface in the solution, and its relationship is also shown in Fig. 3d. As we can see from the figure, the potential drops rapidly when it crosses the interface and enter IHP, then slows down in the OHP and is almost zero as it enters the diffuse layer.

EDL structure can greatly improve device performance because of its huge capacitance. The channel layer and gate can be regarded as a parallel plate capacitor, and its capacitance formula is as follows.

$$C = \frac{\epsilon_0 \cdot \epsilon_r \cdot S}{d} \quad (3)$$

In device design, the electrolyte layer is very narrow, and with the effect of EDL, the actual solution width d is even smaller. Meanwhile, the rough interface greatly expands the actual area S , so the capacitance of the capacitor is very large according to Eq. (3). Then according to the formula (4) as follows.

$$C = \frac{Q}{U} \quad (4)$$

We can see that the small gate voltage signal can also induce many carriers in the channel, thus changing the source-drain current. Therefore, compared to other 3D devices, the most notable feature of OEDLT is its high capacitance, which enables the device to operate at a very low voltage, reducing the thermal loss of the device. However, due to the fluidity of the solution, the stability of the device is greatly reduced, which also limited its application.

Organic electrochemical transistor

Different from OFET, ions in electrolyte of OECT can enter OSC, therefore the corresponding G_m has a form similar to Eq. (2) as following:

$$G_m = \frac{W}{L} \cdot \mu \cdot d \cdot C^* \cdot (V_{th} - V_G) \quad (5)$$

This formula is called Bernard formula (Rivnay *et al.*, 2015; Bernardis and Malliaras, 2007). Here, d is the thickness of the channel and C^* is the capacitance per unit volume in the channel. Compared to the Eq. (2), we can find that only $d \cdot C^*$ replaces C' . As shown in Fig. 3d, The effect of ions on the channel in OECT is not limited to the interface, but the whole channel, so it is more sensitive for gate voltage to the regulation of source-drain current, and greatly increases the G_m of the device (Khodagholy *et al.*, 2013; Paterson *et al.*, 2018).

It is worth noting that the electrochemical doping of OECT is similar to the doping mechanism in inorganic semiconductors. OSC materials do not have lattice periodicity, so the traditional band theory needs to be modified. The frontier molecular orbital theory proposed by Houk can describe the band structure of organic materials (Houk, 1975). In his theory, the Lowest Unoccupied Molecular Orbital (LUMO) is analogous to the bottom of conduction band in inorganic semiconductors, while the Highest Occupied Molecular Orbital (HOMO) is analogous to the top of valence band. For intrinsic semiconductors, there is a large energy gap between the LUMO and HOMO. When the gate voltage is applied, the ions enter the OSC, which is equivalent to inserting the impurity level in the energy band. For P-type doping, the impurity level (acceptor level) is an empty band that energy is lower than the HOMO, where an electron can jump to the impurity level and create a hole to conduct electricity. For N-type doping, the impurity level (donor level) is the full band level higher than the LUMO, which can provide the LUMO with electrons to conduct electricity. The doping mechanism of intrinsic organic semiconductors is shown in Figs. 4a and b. However, the OSC of most OECT devices is P-type semiconductor, and the mechanism of electrochemical doping is compensation doping (Lüssem *et al.*, 2013). In other words, there is a certain acceptor level in OSC, and when gate voltage is not applied, there is a high concentration of hole carriers in the device. While the gate voltage is applied, ions will enter the OSC, which is equivalent to the introduction of

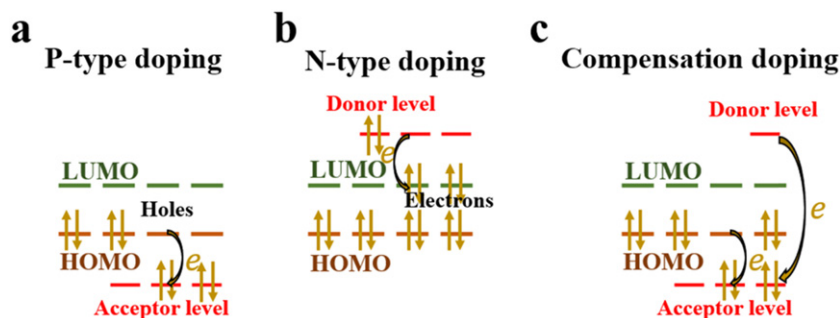


Fig. 4 The schematic diagram of electrochemical doping.

the donor level, and the electrons on the donor level will first recombine with the holes on the original acceptor level, so the carrier concentration decreases, thus achieving the regulation of current. The mechanism of impurity compensation is shown in Fig. 4c.

Among all kinds of ONDs, because of its convenient manufacturing technology, OEET has attracted the most attention, especially for the study of new materials for OEET (Lenz *et al.*, 2019). At present, OSC materials commonly used in OEET devices include PEDOT: PSS, (Elschner *et al.*, 2010; Gkoupidenis *et al.*, 2015) P3HT, (Choi *et al.*, 2020) etc., which can combine with electrolyte ions and have good conductivity. If the solid state ionic gels are applied as gate dielectric, the device stability of organic electrolyte-gate synaptic transistor is much better than that of devices with liquid electrolyte (Rivnay *et al.*, 2018).

Multi-input and Multi-output Structures

The above is an introduction to the principle of a single device. In order for the ONS to be composed by ONDs, the concepts of multi-input structure and multi-output structure were proposed. In real neurons, a cell often has many synapses to connect with other cells, so it can receive signals from multiple cells at the same time, and can also process signals to other neurons. So, OND that mimics a neuron needs to have a similar function. The multi-input and multi-output structure can meet this requirement.

Multi-input Structure

The schematic diagram of multi-input structure is shown in Fig. 5a, where six gates are simultaneously connected with the electrolyte. Because of the difference of distance and angle between each gate and channel, the same signal applied to different gates will lead to different source-drain current. In general, the farther the gate is from the channel, the smaller the source-drain current (Gkoupidenis *et al.*, 2016). At the same time, it has been shown that when different signals are applied to multiple gates at the same time, the current in the channel is a simple superposition of the current when each gate signal acts alone, which is called the superposition principle (Qian *et al.*, 2017b). This result shows that signals are transmitted independently in multi-input structures without interfering with each other, which lays a foundation for simulating signal transmission in biological cells.

Multi-output Structure

The multi-output structure is shown in Fig. 5b, where multiple channels are immersed in the same electrolyte and are simultaneously regulated by a gate. In contrast to the multi-input structure, the multi-output structure simulates the transmission of signals from a single neuron to multiple neurons. Depending on the distance between each channel and the gate, the intensity of source-drain current will be different (Gkoupidenis *et al.*, 2017). In addition, if the channels are of different sizes and materials, different waveforms of source-drain currents can be output. The multi-output structure can realize the signal transmission of multiple lines, so that if the transmission of one line fails, the transmission of other lines can also ensure the accuracy of the signal, which can avoid the signal error in the transmission process as much as possible, and it has a great role in improving the stability and error-tolerance rate of ONS.

Mixed Structure

The mixed structure combines multi-gate structure and multi-output structure, which is closer to the real neuron. As shown in Fig. 5c, three gates are immersed in the same electrolyte to regulate multiple channels. For the three gates, it still satisfies the superposition law described in multi-input structure. As for channels, channels with different sizes of materials can also be used to achieve different types of signal output. Repeated combinations of multi-input structures, multi-output structures, and mixed structures, combined with the logic capabilities of OND devices (described later), we can enable complex ONS (Fu *et al.*, 2018b).

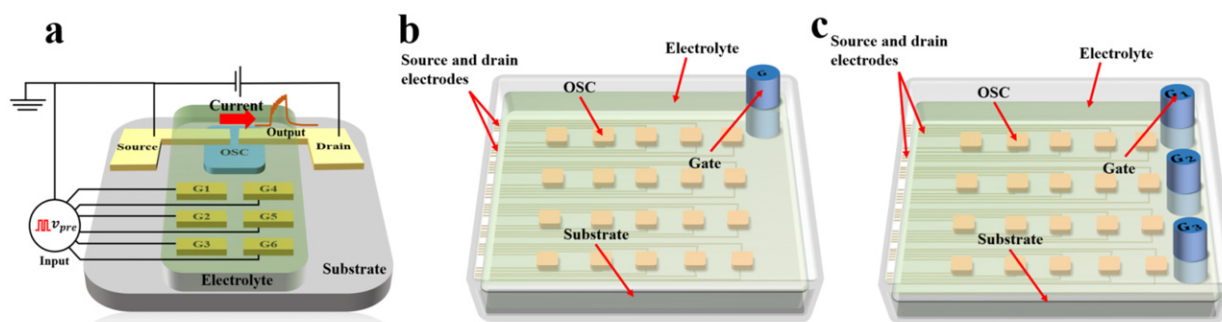


Fig. 5 Schematic diagram of multi-input structure (a), multi-output structure (b) and mixed structure (c).

The Application of ONDs

The OND is rich in variety and performance, with a similar principle to biological synapses, while the organic materials make it a certain degree of flexibility. These advantages make it have a wide application prospect in many fields (Zhang *et al.*, 2020; Sun *et al.*, 2021; Kuzum *et al.*, 2013). Here, we will focus on the application of OND in intellisense, neuromorphic chip and flexible e-skin. All these functions can be integrated into artificial intelligence systems (Pierson and Gashler, 2017) as shown in Fig. 6.

Intellisense

OND can be used as a biosensor, which is currently the main application direction. The basic principle is to convert external information into electrical signals by ONDs (Lee *et al.*, 2018; Kim *et al.*, 2018). For example, Kim *et al.* designed a pressure integrated sensor, (Kim *et al.*, 2020) and its structure is similar to Fig. 6a. Here, pressure can change the contact area between conical ionic gel and top electrode, resulting in a correlation between source-drain current and pressure, which can convert pressure signals into electrical signals to realize pressure sensing. Similarly, with the use of organic photosensitive transistors, optical signals can be converted into electrical signals to achieve artificial vision sensors, (Wang *et al.*, 2018) as shown in Fig. 6b. In 2022, Qian *et al.* have proposed an artificial synapse based on NO_2 by taking advantage of the NO_2 molecule's ability to induce organic heterojunction to produce carriers, (Qian *et al.*, 2022) and the conceptual diagram of NO_2 detection based on this device is shown in Fig. 6c. Perhaps in the future, more gas sensors will be able to detect different gas molecules, enabling an artificial olfactory. The sensors are similar to input of reflex arcs and serve as information capture in ONS. Many sensors are already in our lives, such as autonomous driving and face recognition etc, and we believe there are more excellent intelligent sensors to come in the future for constructing high-performance ONS (Liu *et al.*, 2021; Ielmini and Ambrogio, 2019; Nwakanma *et al.*, 2021; Chen *et al.*, 2020).

Neuromorphic Chip

Neuromorphic chip is a bridge to realize ONS intelligence, and its basic unit is OND. The function of neuromorphic chip is to convert electrical signals into digital signals, and then get output or be stored in memory after processing. Its work depends on the logical functions of OND and the processing of information by the neuromorphic network.

Logic function

The OND's logical function is to convert electrical signals into digital ones. The following illustrates how the logic function is realized by taking a two-gate OECT as an example. Applying voltage at both G1 and G2 can lead to an increase in current (I_D) in the channel. We call the state is ON when a voltage is applied at a gate (assuming the voltage applied is the same), and by the superposition principle of multi-input structures (explained in Section "Multi-input Structure"), if G1 and G2 are ON at the same time, the I_D will be twice as large as if G1 or G2 were ON alone. Based on this, we can realize the logic function of 'AND' and 'OR' by setting the current reference value as shown in the top of Fig. 6d. Specify that if the I_D is greater than the reference value, the output is 1 (the state of ON). Otherwise, the output is 0 (the state of OFF). It can be found that when the reference value is greater than the I_D of only one ON, but smaller than the I_D of two ONs, the two gates constitute the logical relationship of "AND". When the reference value is greater than 0 and less than the I_D that only one ON, then it is the logical relationship of 'OR'. The examples above are two of the simplest logic functions that can be implemented by devices. When multiple gates and multi-output structures are applied, the logic functions can be more complex, forming a variety of logic switches. In addition, scientists have designed logic structures based on light sensing, as well as a hybrid logic of multi-sensory functions (Calvert and Thesen, 2004; Hao *et al.*, 2020). The logic switch function of OND is the basis of realizing neuromorphic chip (Shi *et al.*, 2021; Lee *et al.*, 2021).

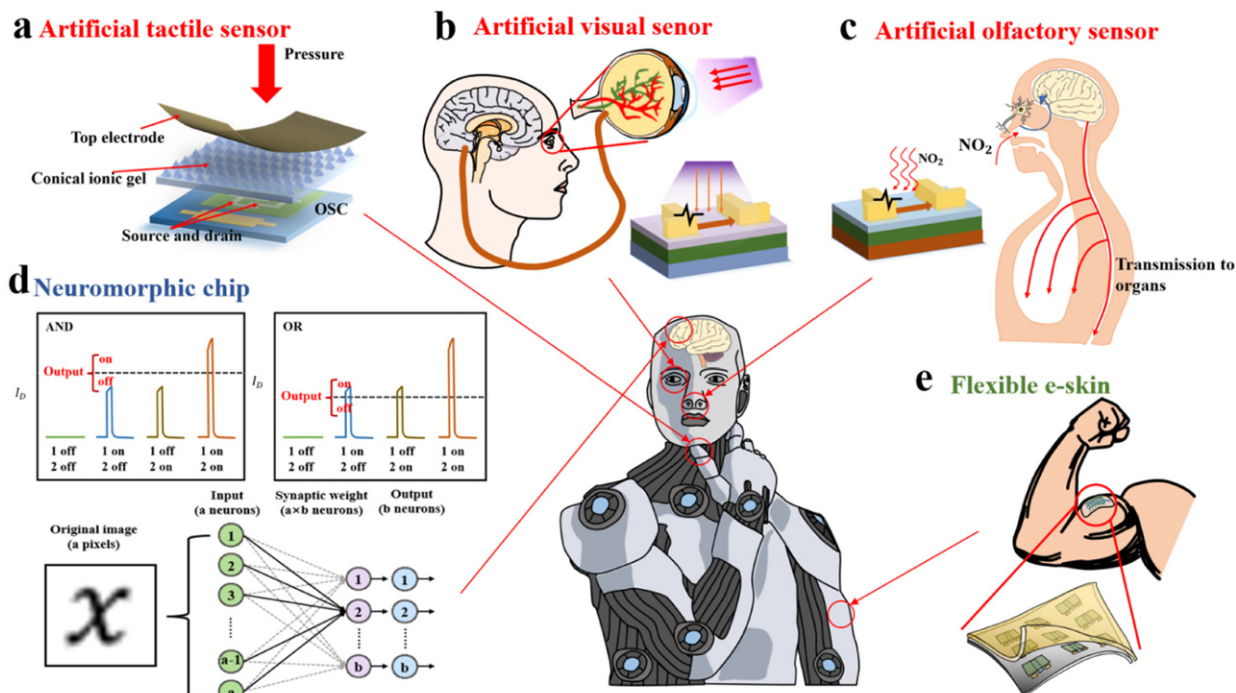


Fig. 6 (a) Tactile sensor designed. (b) Photosensitive sensors can be used for artificial vision. (c) Gas sensors can be used for artificial olfactory. (d) The schematic diagram above shows the logical switches about “AND” and “OR”. The diagram below shows how a neural network processes information. (e) Flexible electronics attached to the skin.

Neural network

From the perspective of device construction, the hardware neural network generally refers to the connection mode of crossbar arrays constructed by the ONDs, and its ability to process information cannot be separated from the cooperation of these devices (Shao *et al.*, 2021). The bottom diagram in Fig. 6d illustrates the flow of neural network signal processing. Each pixel is an optical sensor, and the image information (the letter “x”) is converted into electrical signal by optical sensors. In the neural network, the synapses between the input and output can form complex weight matrix. These logic switches convert electrical signals into digital signals for processing and finally the information is concentrated in few synapses and output, greatly improving the efficiency of information processing and the memory capacity of the neuromorphic chip (Qian *et al.*, 2019).

Flexible e-Skin

The channel and substrate of the OND are organic materials, which provide excellent flexibility, so it also has potential applications in smart clothing and artificial skin (Lee *et al.*, 2018; Xu *et al.*, 2021). For example, Trung *et al.* designed a stretchable OND array showed in Fig. 6e, (Trung *et al.*, 2016) which can be attached to the skin to detect temperature and heart rate in real time, allowing for the design of an intelligent skin. In medical, biologists have been able to biologically grow stem cells to produce a small piece of skin, but it lacks hair follicles. If many of the tiny ONDs are integrated on a flexible substrate, researchers may be overcome these obstacles in the future by creating artificial skin (Lee *et al.*, 2019; Yu *et al.*, 2019; Wang *et al.*, 2021).

Summary

In this chapter, we first introduce the classification and development history of neuromorphic system, then introduce the synaptic function of biological synapses. Next, we describe how some types of 2 T and 3 T ONDs work, and detail how these devices construct into multi-input structures and multi-output structures. Finally, we introduce the current research progress and application fields of ONS and look forward to its future development.

Although the studies about OND have made great progress, it still faces some difficulties and challenges. Firstly, the studies on how OND constitutes ONS need to be further studied, and there are not enough theoretical studies on the learning mechanism of ONS. Second, at present, most organic materials are P-type doping, and the organic materials of

N-type doping need to be further explored. Thirdly, although the multi-input structure and multi-output structure are very similar to the neural network of the brain, it still faces many difficulties. For example, it needs further research that how to use multi-input structure and multi-output structure to realize computation, memory and learning of human brain. Finally, compared with traditional inorganic devices, OND is unstable and sensitive to environmental effects, which requires further exploration.

In general, OND is a very promising research field, which is developing rapidly due to the emergence of new materials and new structures. In addition, the OND has achieved excellent sensitivity and response time nowadays, but its stability needs to be improved. However, with the demand for smart devices increases and the concept of the metaverse becomes more widespread, we believe ONS constructed by OND will be one of the most attractive research areas in the coming decades.

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Nanoscale 3D Printing

Monsur Islam, Stefan Hengsbach, Dario Mager, and Jan G Korvink, Karlsruhe Institute of Technology, Institute of Microstructure Technology, Eggenstein-Leopoldshafen, Germany

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Abstract

3D printing has provided a pathway for the rapid and inexpensive fabrication of three-dimensional components of a variety of materials, useful for a wide range of applications. Even though 3D printing is in the advanced stage at the macroscopic level and has progressed tremendously in producing 3D objects with a sub-millimetric resolution, 3D printing in the nanoscale is still in its infancy due to current technological challenges. However, currently available 3D nanoprinting technologies have already demonstrated the fabrication of 3D architectures, exhibiting novel and superior functionalities and proof-of-concept applications. This article provides a closer look at the most promising 3D nanoprinting technologies by discussing their working principle, achievable architectural features, and already demonstrated applications. It also briefly discusses the current limitations, to illustrate a road map for future technological advances.

Key Points

- A definition of 3D nanoprinting and its current scope have been discussed.
- A general principle of 3D nanoprinting has been presented, which has led to categorizing the current technologies of 3D nanoprinting.
- Different 3D nanoprinting technologies have been reviewed, given their working principles, capabilities, and current applications.
- The limitations of the 3D nanoprinting technologies and their future direction have been discussed.

Introduction

Additive manufacturing, popularly known as 3D printing, refers to the "bottom-up" technologies for fabricating arbitrary 3D shapes, typically in a layer-by-layer fabrication approach. 3D printing has already had a massive impact at the macro-scale, for rapid prototyping and low-volume production in several areas, including health, energy, construction, automotive, aerospace, and entertainment (Yan *et al.*, 2018; Tay *et al.*, 2017; Liaw and Guvendiren, 2017; Muralidhara and Banerjee, 2021; Lim *et al.*, 2016). The feasibility of rapidly transforming a 3D computer-aided design into 3D physical component with the freedom of design without the need for any mold is a major advantage of 3D printing, among many others. Furthermore, the emergence of innovative 3D printing technologies has enabled the direct writing of a variety of materials, including polymers, metals, ceramics, and composites. However, 3D printing at the nanoscale is still in its infancy, even though the 21st century is considered the era of nanotechnology.

Following the widely accepted definition of nanomaterials, (Kreyling *et al.*, 2010) 3D nanoprinting should also be defined as the technology that enables 3D printing with a sub-100 nm resolution, at least in one direction, without any subtractive removal (Engstrom *et al.*, 2014). The structures obtained from 3D nanoprinting can exhibit surprisingly rich and programmable properties, which can have a significant impact on various fields ranging from energy devices to biomedical applications. The properties of the final product strongly depend on the constituent materials, and the control and precision of the nano-structural material in 1-, 2- or 3-dimension. The definition of 3D nanoprinting excludes several thin-film technologies, such as atomic layer deposition and molecular beam epitaxy, despite offering nanometric resolution and high control, as they are predominantly used for 2D patterning. They can certainly be integrated with other 3D printing technologies to enhance the functionalities of the 3D printed objects, but they can not enable 3D structuring by themselves. The definition of 3D printing also limits currently available technologies, as only a very few technologies can facilitate 3D printing with a sub 100 nm resolution. Few other technologies, including inkjet printing and aerosol jet printing, can facilitate layer-by-layer structuring with sub-micron feature sizes. Therefore, here we also include these technologies to provide a bit wider perspective of 3D nanoprinting technologies. On the other hand, a few other printing technologies, such as electrohydrodynamic printing, (Sadaf *et al.*, 2022; Park *et al.*, 2019) and stereolithography, (Islam *et al.*, 2020; Katsuyama *et al.*, 2022) have demonstrated 3D printing with the resolution of a few microns, which we do not include in the current list of 3D nanoprinting technologies. With further technological development, these methods have the potential to be evolved as 3D nanoprinting platforms in the near future with a sub-micron or higher resolution. For example, electrohydrodynamic printing, particularly electrospinning, which generally creates randomly distributed nanofiber mat, can enable the fabrication of nanofibers with a diameter down to sub 10 nm (Deng *et al.*, 2020; Jian *et al.*, 2018). However, 3D structuring with electrospinning still has not reached such a high resolution due to the current technical limitations while transforming it to a 3D printing platform.

In this article, we categorise the 3D nanoprinting technologies into two main groups. The first one is isotropic voxel printing, where the nanoprinting resolution can be achieved isotropic in all three dimensions, resulting in nanoscale features in all three dimensions as well.

Table 1 Overview of typical used objectives for 2PP, and their parameters in combination with a Nanoscribe Photonic Professional GT2[®], using light with a wavelength of 790 nm

Objective	Magnification	Min. Voxel Width	Min. Voxel Height	Aspect Ratio Voxel	Working Distance	Printing Field $\tilde{A}$
Zeiss Planapochromat	100 $\times$ NA 1.3	150 nm	360 nm	2.6	360 μm	140 μm
Zeiss Planapochromat	63 $\times$ NA 1.4	340 nm	826 nm	2.8	360 μm	200 μm
Zeiss Planapochromat	25 $\times$ NA 0.8	595 nm	33.0 μm	5.6	380 μm	400 μm
Nanoscribe	10 $\times$ NA 0.3	1600 nm	25.4 μm	16.0	700 μm	1000 μm

Note: Reproduced from Fischer, J., Wegener, M., 2013. Three-dimensional optical laser lithography beyond the diffraction limit. *Laser & Photonics Reviews* 7 (1), 22–44.

The second category is referred to as flat 3D printing, where the nanoscale resolution is achieved mainly within the layer thickness and one or both planar directions feature micro or macro scale dimensions. The following sections describe each of these 3D nanoprinting technologies, discussing their operating mechanisms, achievable structural features, and their already demonstrated applications.

Isotropic Voxel Printing

Isotropic voxel printing works using a general principle similar to macroscopic 3D printing, where the printing method transforms a computer-aided design into a 3D object using their respective methodologies. Currently, there are only two technologies available which can facilitate 3D isotropic voxel printing with nanoscale resolution. These are two photon polymerization and focused electron beam induced deposition.

Two Photon Polymerization

Two photon polymerization (2PP) facilitates the controlled fabrication of 3D structures with typical feature sizes in the range of 150–200 nm (Fischer and Wegener, 2011). 2PP uses a laser beam with high pulse power and a narrow focal point to crosslink a highly defined volume of a photoresist at the focal center of an objective. Since a photochemical reaction only happens at the focus point, 3D structures can be fabricated by moving the focus point relative to a substrate. Even smaller feature sizes in the range of 55 nm can be achieved by stimulated emission depletion (STED) (Wollhofen *et al.*, 2013). Here a second light source is used for two-photon excitation at the outer shape of the voxel. However, due to the high complexity in terms of optical alignment and the a limited volume which can be fabricated there are no commercial lithography systems available up to date.

Working principle

2PP typically uses a laser wavelength of around 790 nm, while the photoresist is typically sensitive to light at half of this wavelength. This means that the photo-crosslinking of the photoresist does not start, even after it is exposed to light. This is because the energy of a single photon is not high enough for photo-crosslinking. A photochemical reaction for crosslinking can only happen when a laser beam with a high peak power focuses at a narrow focal point, facilitating two-photon absorption by the photoresist molecules. This acts like a frequency doubling or respectively wavelength halving for the photoresist in comparison to the light femtosecond light.

Since the energy density is the highest at the focus point and decays with $1/e$ from the center the resulting volume can also be smaller than the optical resolution of the used objective. A threshold under which no polymerization is possible limits the minimum achievable voxel size. By increasing the laser power also, the voxel size increases linearly until a point where multiple photons are absorbed and other nonlinear reactions happen. This leads to overreactions in the resist (Baldacchini, 2016). The size of the voxel can also be adapted by the choice of a suitable objective for focusing. Table 1 gives an overview of common objectives and the voxel size, which can be archived. It should be noted that this is not forced to be the smallest possible feature size. As shown in the table, higher magnifying objectives have smaller voxel heights because the cross-section of the beam is smaller due to the larger numerical aperture (NA). To achieve the highest possible resolution, mostly immersion objectives are used, where the objective is dipped into the photoresist. This is also known as Dip-in Lithography (Fig. 1).

In principle, every material that is photosensitive at the stated wavelength can be used. However, to achieve the best possible voxel size, light guidance in the printing material is also important. This means that the refractive index of the photoresist has to match the used objective. This is the case for most of the available commercial photoresists, which aim for the highest resolutions. These resists are also chemically optimized and tailored for the best sensitivity for 2PP processes as well as for low shrinkage. Most commercial photoresists are polymers, but there are also glass-type photoresists and polydimethylsiloxane (PDMS) Fig. 2 shows an example. Even resists tailored for special applications like optics, bio-applications or mechanic applications are available. Even if many materials for special needs are available right now, these come often with the drawback of a small processing window. This makes it necessary to find the right process parameters by iteration.

Since the polymerization happens only at the focus point of the laser, the laser beam needs to scan to achieve a complex structure. This can be done by integrated piezo- or motor stages. To achieve high speeds, the common way is to use a Galvo scan unit. This unit is placed in the beam of the setup. The two integrated mirrors are able to scan the beam very quickly, up to 200 mm/s in the field of

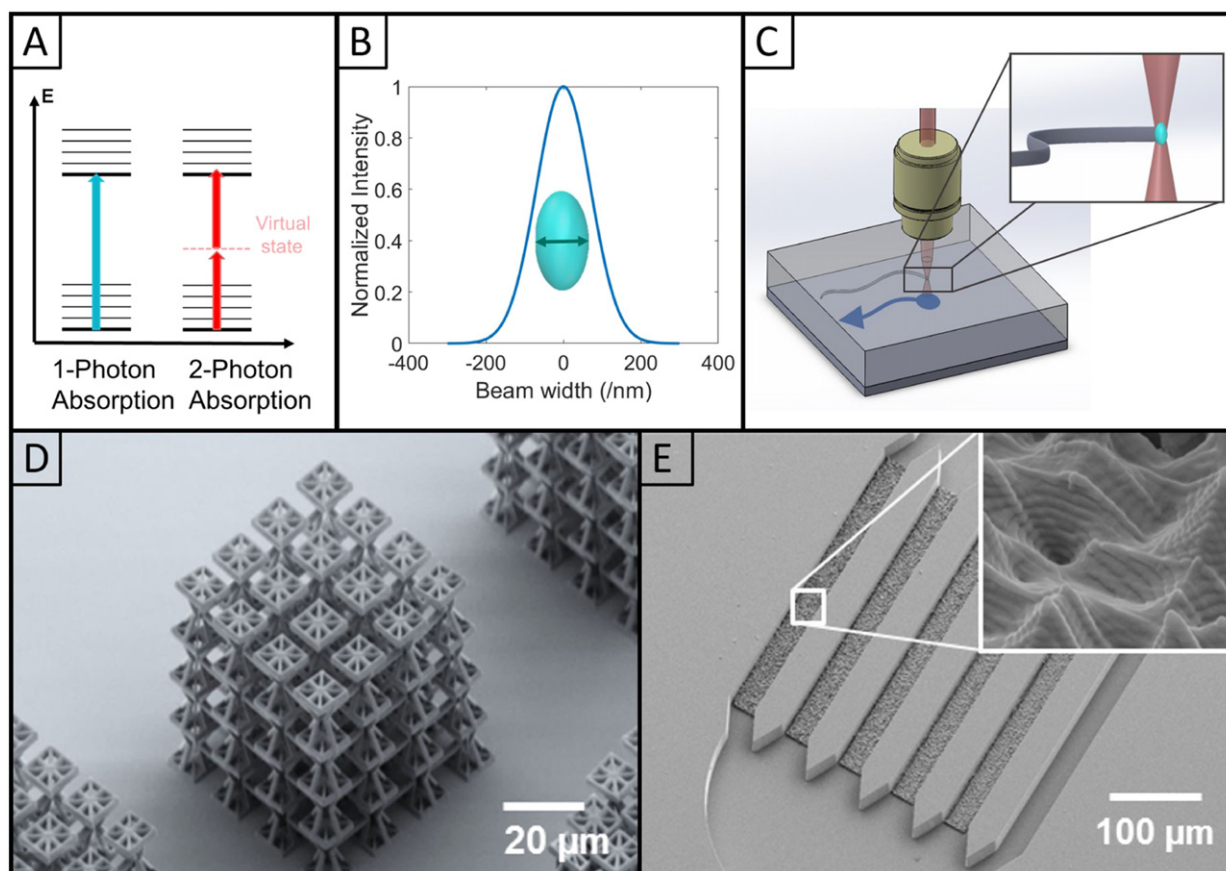


Fig. 1 (A) Working principle of 2PP; In comparison to one photon absorption (blue), where the energy of a photon is high enough for a photochemical reaction, two photon absorption (red) only leads to a photochemical reaction if two photons come together (B) The energy density is only at the focal point high enough to initiate the crosslinking of the photoresist. Also, the possibility decreases in the volume with the Gaussian profile of the laser. A minimum threshold is needed for a reaction. (C) lateral movement can be used for structuring. This can be done by weather scan the sample or the beam within the FOV of the objective. (D) Example of an auxetic structure fabricated using 2PP. The overall dimension of the structure is $40\ \mu\text{m} \times 40\ \mu\text{m} \times 40\ \mu\text{m}$, with the width of single lattice element of $150\ \text{nm}$. (E) Combination of 2PP with conventional lithography to form a fluidic system. 2PP had been used to add fractal surfaces inside of channels with a minimum feature size of $1\ \mu\text{m}$. Reproduced from Hengsbach, S., Lantada, A.D., 2014a. Direct laser writing of auxetic structures: Present capabilities and challenges *Smart Materials and Structures* 23, 085033S. Hengsbach, S., Lantada, A.D., 2014b. Direct laser writing of fractal surfaces: Strategy to design and manufacture textured materials. *Advanced Engineering Materials* 17 (2), 172–180.

view of the objective (FoV). This allows very fast lateral scanning. To build up the structure, the focus plane has to be shifted with a piezo or a motorized stage. To achieve structures which are larger than the FoV, lateral stages are used for stitching. The printing time of 2PP depends on the structural feature size, the chosen objective for printing, structural complexity, and the size of the structure.

Due to the small sizes, the structures need to be fixed to substrates during fabrication. Typically substrates are glasses, such as fused silica or soda lime, but also other materials like metals, ceramics, or even PCB can be used. Even if nearly any material can be used, there are two points to consider. To attach the structures to the substrate, the interface has to be detected. This is done optically by detecting a reflection or, in other words, a change in refractive index. Since the photoresist is already adapted to match the needs of the objective in terms of refractive index, the substrate must differ from this. For non-transparent substrates, this is normally no problem but if they have a rough surface, the light will be scattered and exposure will be difficult. In addition, there might be an issue with reflections at the interface, which cause destructive interference and distortions in the shape of the structures. The other important point concerning the material is adhesion. Polymers shrink around 5%–10% during development, which causes high friction against the substrate. Especially if the surface is flat (e.g., glass, gold), large structures tend to delaminate. To improve the adhesion the substrate can be pre-treated using the following techniques:

- Cleaning with acetone and isopropanol (IPA): A clean substrate is the key to good structures. The chemicals remove contaminant particles, such as dust or residues from dicing (in case the substrate had been reshaped), from the substrate surface. However, the substrate has to be prepared also with one of the following steps.
- Oxygen plasma: Typically, plasma oxidation is performed for the substrate to remove humidity and organic substances from the surface. The parameters of the plasma oxidation depend on the nature of the substrate.

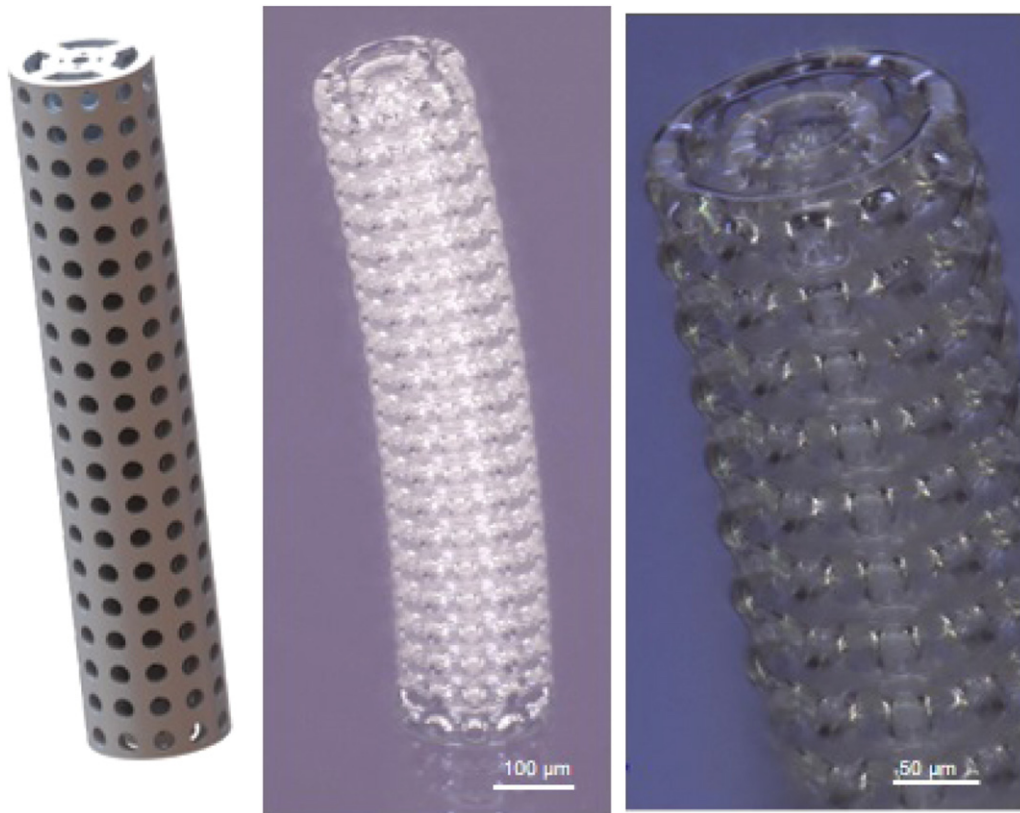


Fig. 2 Example of a PDMS structure fabricated with 2PP-Lithography using IP-PDMS (Nanoscribe GmbH) (middle). The left picture shows the computer-aided design of the structure. The height of the structure was 1 mm, the diameter was 200 μm , and the diameter of the holes at the sidewalls was 30 μm . The middle image shows the fabricated structure, and the right picture shows the high-magnification image, showing the details of the structure. The edges are rounded but very defined.

- Heat treatment. Humidity can also be removed by heating the substrate. A typical procedure for heat treatment includes heating on a hotplate at 110°C for 15 min.
- Silanisation: While the former methods offer a physical improvement, a chemical bonding between the substrate and the resist can also be used. For example, a solution of 1% Trimethoxysilylpropylmethacrylate in 95% Ethanol and 5% Water (ph adjusted to 4.5–5.5 with acetic acid) enhances the adhesion between the photoresist and a glass substrate.

Applications

The possibilities 2PP offers are nearly endless, because this technology gives the user true 3D freedom in design. Even if there are still limitations to the technology, these are more related to the current capabilities of lithography systems. The following are some brief examples of applications.

One of the popular applications of 2PP is the fabrication of mechanical metamaterials featuring nano lattice elements (Bauer *et al.*, 2017). Metamaterials are synthetic materials which are designed to exceed the properties of materials found in nature. 2PP allows the fabrication of nano lattice elements, that outperform the mechanical properties of macro or micro-scale lattice. Furthermore, a post-processing step allows the transformation in other materials beyond the photoresist. For example, glassy carbon nano lattices can be achieved through the carbonisation of 2PP-fabricated nano lattices (Bauer *et al.*, 2016; Zhang *et al.*, 2019). During carbonisation, a significant geometrical shrinkage occurs (up to 85%, depending on the precursor geometry and the choice of precursor), (Cardenas-Benitez *et al.*, 2019) which further enhances the resolution of the fabrication method. An example of such carbon nano lattice metamaterial is presented in Fig. 3 (Bauer *et al.*, 2016). The fabricated carbon nano lattices exhibited mechanical strength up to 3 GPa, which is close to the theoretical limit of the strength of glassy carbon.

2PP can also be used for optical applications. As an example, optical wirebonds shall be mentioned. One of the biggest challenges in telecommunications is the energy consumption. In our days, nearly half of the energy in communications (e.g., servers) is used for cooling to get rid of warmth produced by electrical elements. This could be decreased significantly if the conversion from optical to electrical and back to optical signals can be shortened by a direct optical link. Analog to wire bonding, which is used in electronics for inter-chip connections, optical wirebonding based on 2PP can be used. Fig. 4 shows an example of the bonding from a fiber with four cores to a chip with integrated wirebonds. To connect, the components are detected and an

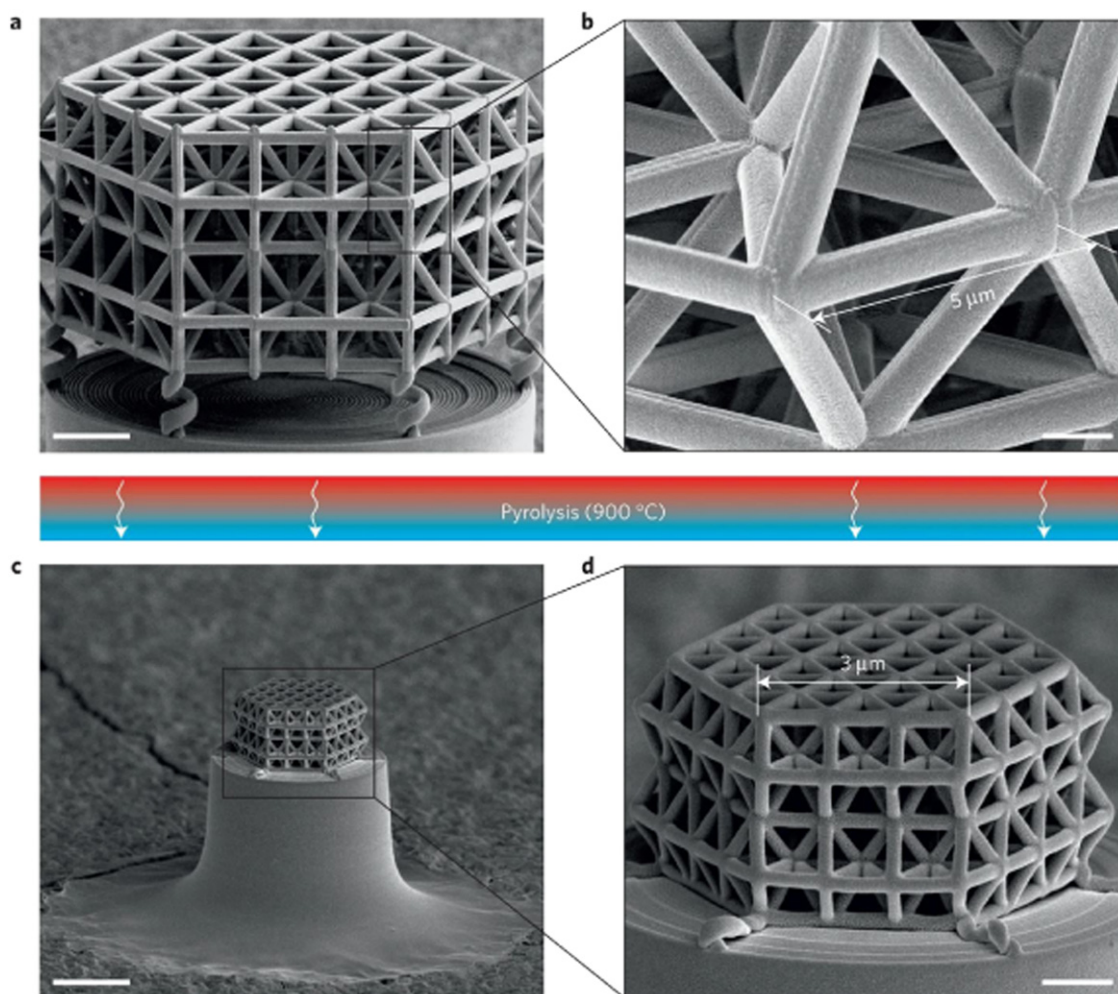


Fig. 3 a,b, Polymer structure before pyrolysis: whole structure (a) and close-up view of a single unit cell (b). c,d, Facilitated by a supporting construction, which decouples the structures from the substrate, the nano lattices isotropically shrink to about 20% of their initial size during pyrolysis. The magnifications of a and c (scale bars 5 μm), and also b and d (scale bars 1 μm), are identical. Reproduced from Bauer, J., Schroer, A., Schwaiger, R., Kraft, O., 2016. Approaching theoretical strength in glassy carbon nanolattices. *Nature Materials* 15 (4), 438–443.

optimized geometry for the waveguides is calculated. After an alignment and fabricating of the waveguides, a seamless optical link is formed. The coupling losses are as small as 1.7 dB (Lindenmann *et al.*, 2015).

Even if the polymer material used for 2PP is not bio-compatible, the technology can be used for a large variety of applications in this field. Of common interest is the need to tune surface wettability to specific needs. These can be reached by giving surfaces a designed structure. As an example, the surface of the lotus leaf can be mentioned. This surface can also be replicated by 2PP. The properties can be even more enhanced by giving the structure a substructure like shown in Fig. 5.

Focused Electron Beam Induced Deposition (FEBID)

Focused electron beam-induced deposition (FEBID) is, as the name suggests, a technique that allows patterning on a surface by highly localized material deposition enabled by a focused electron beam. The patterns are directly defined on a substrate by scanning a focused electron beam over the substrate in the presence of a precursor gas. The advantage of FEBID is no pre- or post-treatment is needed. Typically a scanning electron microscope (SEM), equipped with a gas injection nozzle, is used for FEBID. Typically SEM with a focused ion beam (FIB) avails such gas injection module. An electron beam in SEM can be focused to a spot size ranging from micrometers down to sub-angstrom level, enabling FEBID patterning in nanometric length scale.

Working principle

Fig. 6(a) schematically presents the working principle of FEBID 3D printing. In FEBID, the focused electron beam of SEM is used as the writing tool, whereas the gas injection nozzle is utilized for localized precursor delivery for additive nano-printing. The nozzle continuously supplies gaseous precursor molecules to the substrate surface. A fraction of the impinging flux gets physisorbed on

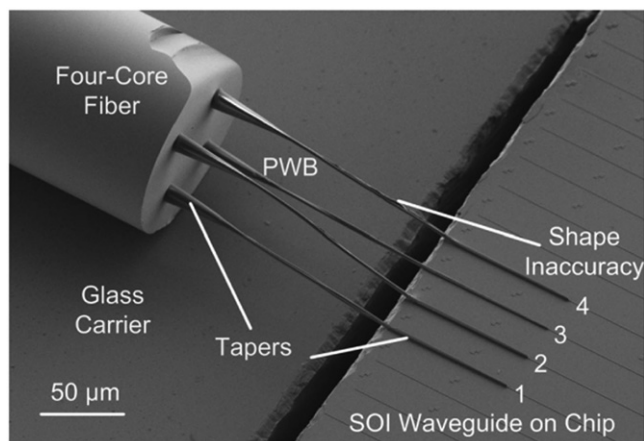


Fig. 4 Fabricated sample: Photonic wire bonds (PWB) connect the individual cores of a four-core fiber to different on-chip SOI waveguides. The PWB are tapered both on the MCF and on the SOI waveguide side to match the mode diameter to that of the fiber core and of the SOI WG, respectively. The PWB consist of a negative-tone photo-resist. At PWB 4, shape imperfections can be seen. Reproduced from Lindenmann, N., Dottermusch, S., Goedecke, M.L., *et al.*, 2015. Connecting silicon photonic circuits to multicore fibers by photonic wire bonding. *Journal of Lightwave Technology* 33 (4), 755–760. Available at: <https://doi.org/10.1109/JLT.2014.2373051>.

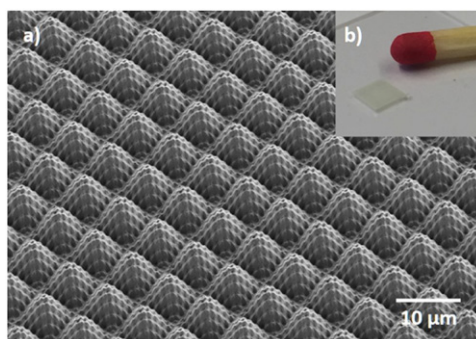


Fig. 5 Larger lotus-inspired surface prototype (3.3 mm — 3.3 mm) for wettability testing a) shows the structures in detail. The bumps of the structure are $10\ \mu\text{m} \times 10\ \mu\text{m} \times 10\ \mu\text{m}$. the sub-nm texture on the surface has been designed to archive a large contact angle. A contact angle of 119° could be archived. Reproduced from Lantada, A.D., Hengsbach, S., Bade, K., 2017. Lotus-on-chip: Computer-aided design and 3d direct laser writing of bioinspired surfaces for controlling the wettability of materials and devices. *Bioinspiration Biomimetics* 12 (6), 066004.

the substrate surface, which diffuses on the surface for a finite time. If the residence time of the precursor molecules is long enough, the primary, secondary, and back-scattered electrons of the focused electron beam interact with the adsorbed precursor, leading to the dissociation of the molecules. The dissociation results in volatile fragments that are removed by the vacuum pumps of SEM, whereas the non-volatile components stick to the substrate, resulting in a highly localized deposition. At this point, the interface of interest switches from the electron beam to the surface to the electron beam to the deposit surface.

A vertical pillar is obtained when a stationary electron beam is used due to the highly localized nature of the deposition and the absence of any lateral movement. However, introducing a controlled relative movement between the electron beam and substrate can lead to the fabrication of innovative and interesting 3D complex architectures. Towards obtaining 3D complex architectures, a moving beam is more advantageous to a moving stage. Fabrication using a moving stage is generally achieved by using the rotating and tilting functions of the stage. However, this process is time-consuming as it requires refocusing of the electron beam at every step of the stage. On the contrary, a moving beam allows for more degrees of freedom. A moving beam is achieved by beam deflection coils, which facilitate precise movement of the beam with a patterning velocity down to tens of nanometers per second. Such a small beam velocity can further facilitate the patterning of free-standing structures. Furthermore, precise movement of the electron beam in the lateral plane and controlled exposure of the electron beam allows the fabrication of complex architectural features, including curved wires and multi-branch structures.

The material patterned in 3D-FEBID depends on the choice of precursor gases. As a high gas influx is required for 3D-FEBID, the precursor is preferred to have a high vapor pressure. To date, a variety of materials, including electrically conductive, semiconductive, insulating materials, and magnetic materials, have been demonstrated for 3D-FEBID. Fig. 6(b) shows a list of current materials that have been demonstrated for 3D-FEBID. However, highly complex structures of insulating materials are often challenging due to the charging effect and localized heating caused by low thermal conductivity. Another disadvantage during fabrication is the incorporation of

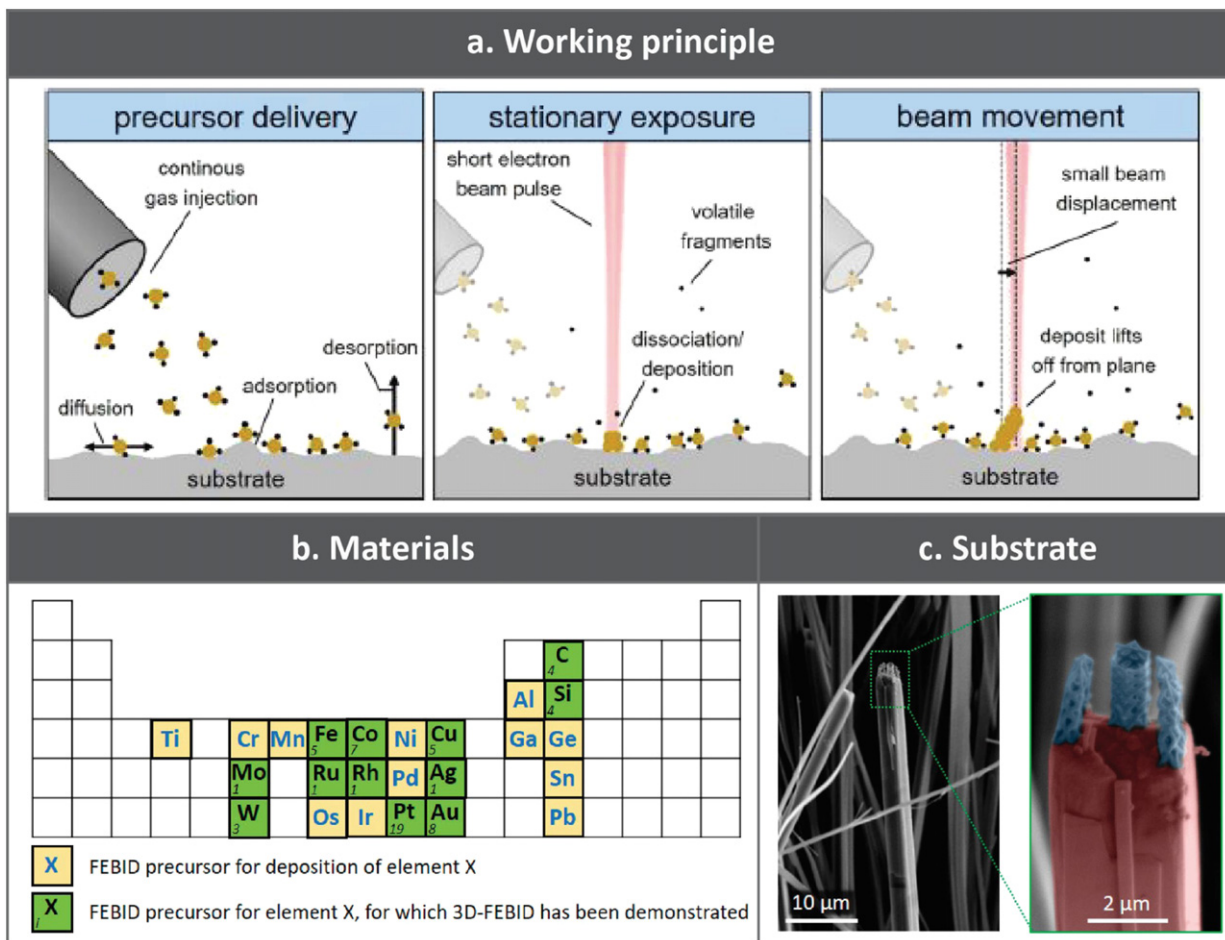


Fig. 6 (a) Working principle of FEBID. (b) Periodic table demonstrating the materials for 3D-FEBID. The "green" materials represent the ones, which are already demonstrated for 3D-FEBID. The "yellow" materials are demonstrated for 2D-FEBID, but ideally, they can be also used for 3D-FEBID. (c) 3D nano-towers of Pt-C fabricated on top of mineral wires using 3D-FEBID, demonstrating the applicability of arbitrary substrate in 3D-FEBID. Reprinted with permission from Plank, H., Winkler, R., Schwalb, C.H., *et al.*, 2019. Focused electron beam-based 3d nanoprinting for scanning probe microscopy: A review. *Micromachines* 11 (1), 48. Winkler, R., Schmidt, F.-P., Haselmann, U., *et al.*, 2017. Direct-write 3d nanoprinting of plasmonic structures. *ACS Applied Materials & Interfaces* 9 (9), 8233–8240. Winkler, R., Fowlkes, J.D., Rack, P.D., Plank, H., 2019. 3d nanoprinting via focused electron beams. *Journal of Applied Physics* 125 (21), 210901. Copyright 2017 American Chemical Society.

impurities within the printed materials, which are originated during the dissociation of the precursor material. The impurity molecules often mask the desired interface, causing undesired geometrical features or poor properties of the printed structures.

3D-FEBID-based patterning is not limited to flat surfaces. Due to the highly localized deposition site, 3D-FEBID can be performed on any arbitrary substrate, which is extremely challenging for any other nanoprinting technology. [Fig. 6\(c\)](#) presents an example, where Pt-C 3D nano-towers were fabricated on top of mineral wires ([Winkler *et al.*, 2017](#)). The only requirements for the substrate are electron-beam and vacuum compatibility.

3D nanoprinted architectures

As mentioned earlier, a stationary electron beam and stage configuration results in the fabrication of vertical pillar structures, which is the most basic architecture in 3D-FEBID. Even though a cylindrical pillar is expected, the pillars fabricated in 3D-FEBID feature four distinctive regions: (1) base region, (2) cylindrical shaft, (3) conical top, and (4) apex. An example of such a pillar is presented in Fig. 7(a), where a gold nano-pillar was fabricated using Me2Au(acc) as the precursor material. The base region often becomes wider than the cylinder shaft part due to enhanced lateral deposition rate at the substrate arising from the stronger precursor diffusion. This is beneficial as it improves the adhesion between the substrate and the final printed structure, providing the entire structure with good mechanical stability. The cylindrical shaft basically exhibits a high degree of parallelism ($\Delta\alpha < 2^\circ$), constructing the pillar-like feature. The typical diameter of the cylindrical shaft ranges from 20 to 100 nm (Plank *et al.*, 2019). The length of the cylindrical shaft depends on the deposition time. With precise deposition, an aspect ratio > 100 can also be achieved. The energy of the electron beam determines the length and shape of the conical top part, as evidenced from Fig. 7(a). Typically a sub-10 nm apex can be achieved in 3D-FEBID, particularly with a low beam current (< 100 pA).

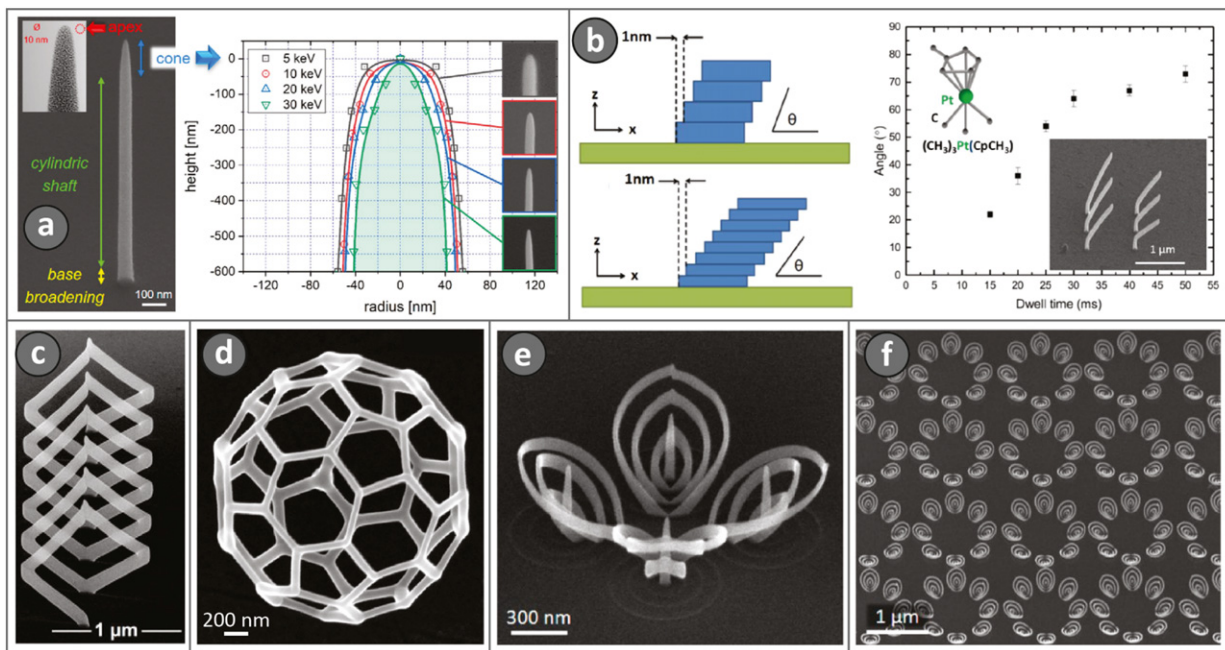


Fig. 7 (a) An example of 3D pillar fabricated using 3D-FEBID, showing different regions of the pillar and how the profile and dimension of the apex depend on the electron beam energy. (b) Left: A schematic of a sequence of vertical growth and lateral pitch in 3D-FEBID, enabling the fabrication of angular structures. Right: the effect of vertical growth duration in determining the angle of the angular structures. (c-e) Examples of 3D architectures fabricated using 3D-FEBID. (f) A series of 3D architectures fabricated using 3D-FEBID, showing the scalability of the process. Reprinted from Plank, H., Winkler, R., Schwalb, C.H., *et al.*, 2019. Focused electron beam-based 3d nanoprining for scanning probe microscopy: A review. *Micromachines* 11 (1), 48. Sanz-Hernández, D., Hamans, R.F., Osterrieth, J., *et al.*, 2018. Fabrication of scaffold-based 3d magnetic nanowires for domain wall applications. *Nanomaterials* 8 (7), 483. Keller, L., Huth, M., 2018. Pattern generation for direct-write three-dimensional nanoscale structures via focused electron beam induced deposition. *Beilstein Journal of Nanotechnology* 9 (1), 2581–2598.

Apart from vertical pillars, lateral movement of electron beam leads to the formation of lateral nanowires. Combination of vertical and lateral growth further results in three-dimensional patterns. For example, scanning along a straight line, with sequential horizontal movement with a pause for vertical growth, leads to 3D angular structures (Sanz-Hernández *et al.*, 2018; Winkler *et al.*, 2018). The ratio between horizontal pitch and vertical growth defines the angle (θ) of the angular structure. Fig. 7(b) shows examples of such angular structures with 1 nm horizontal pitch with varying vertical growth time (Sanz-Hernández *et al.*, 2018). Programmed assembly of multiple angular patterns further leads to several complex 3D architectures. Fig. 7(c-e) show a few examples of 3D complex architectures fabricated using 3D-FEBID.

Applications

Due to the capability of fabricating pillar structures of mechanically stiff materials, 3D-FEBID has been explored successfully for fabricating atomic force microscopy (AFM) tips enabling high-resolution imaging. Several materials have been demonstrated for such purposes, including carbon, silicon, platinum, cobalt, iron, and alloys (Brown *et al.*, 2013; Chen *et al.*, 2006; Jaafar *et al.*, 2020; De Teresa *et al.*, 2016). Apart from fabricating an entire AFM tip, 3D-FEBID is often used for fabricating additional high aspect ratio features on commercially available AFM tips (Fig. 8(a)). Such modifications allow higher lateral and deeper resolutions. For example, a 3D-FEBID-fabricated platinum nanostructure on a commercial AFM tip enabled penetration ~ 200 nm deeper than the commercial tip while scanning tightly packed polystyrene spheres, which further resulted in improved lateral resolution due to the improved penetration (Fig. 8(a)) (Brown *et al.*, 2013). The tip add-ons of chemically inert materials, such as carbon and silicon, also enabled such improved performance in liquid media (Chen *et al.*, 2006). Apart from classical AFM, 3D-FEBID structures also enabled other modes of AFM, depending on the 3D-FEBID material. For example, a platinum tetrapod nanoprobe fabricated at the tip of a commercial AFM tip enabled the scanning thermal probe microscopy, where the contact between the platinum probe and the sample resulted in a change in the electrical resistivity depending on the substrate temperature (Sattelkow *et al.*, 2019). An example of such imaging is shown in (Fig. 8(b)).

Due to nanometric feature size s , actuation of 3D-FEBID structures can be achieved through external stimulation, such as mechanical actuation, magnetic field for magnetic 3D-FEBID structures, (Vavassori *et al.*, 2016) or electrical field for electrically conductive 3D-FEBID structures. Such nanoactuators can be further utilized for sensing applications. For example, Arnold *et al.* (2018) demonstrated gas sensing application using electrically actuated 3D-FEBID-fabricated Pt-C structures (Arnold *et al.*, 2018). The Pt-C nanostructures were brought into mechanical resonance through AC electrical field. The mechanical resonance behavior changed when gas molecules got adsorbed onto the structures, resulting in the gas sensing activity, as shown in Fig. 8(c).

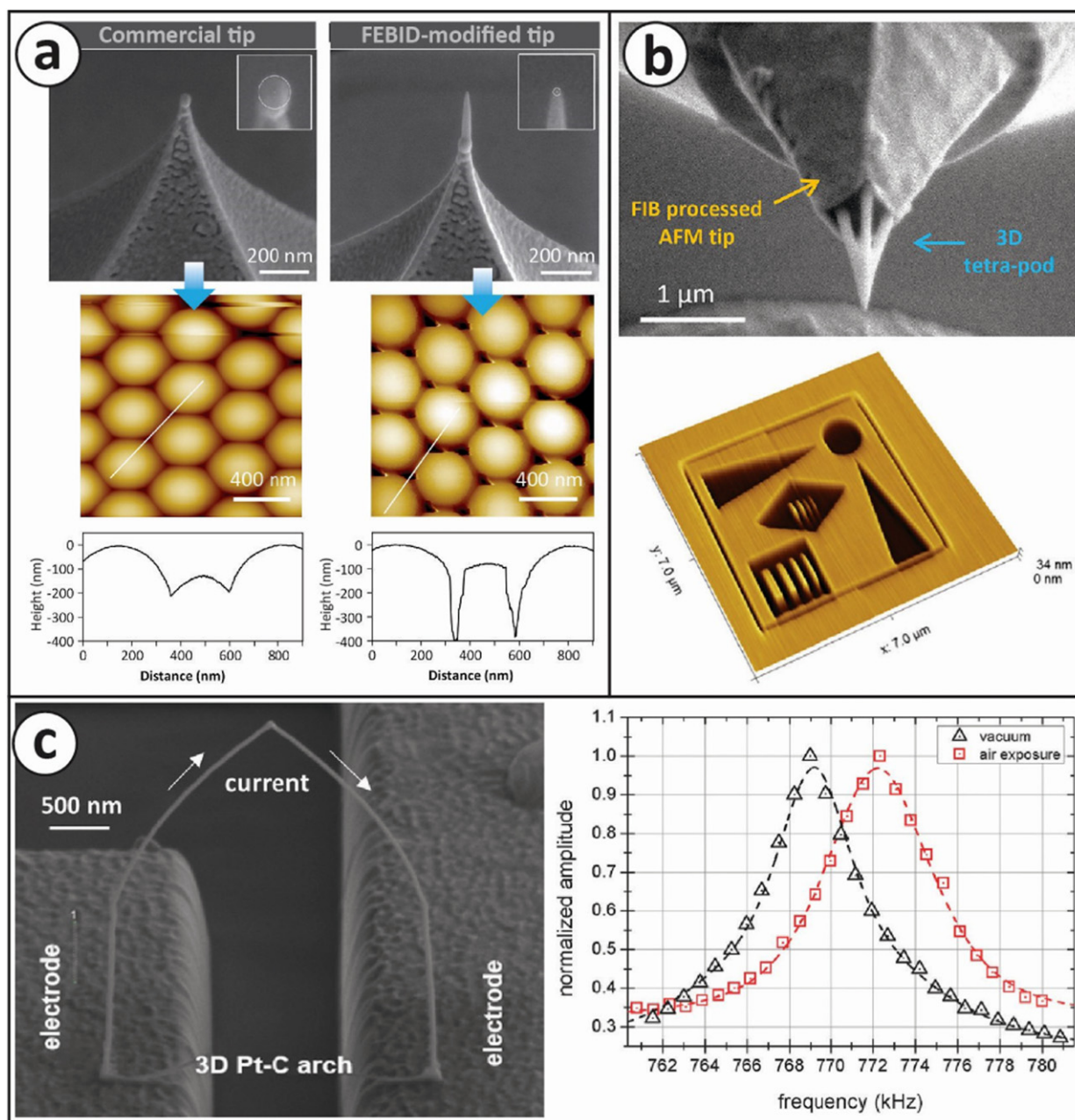


Fig. 8 (a) Left column presents an SEM of a commercial Si AFM tip, an AFM image of tightly packed polystyrene spheres produced by it, and the measurements obtained from it. The right column shows a platinum nanopillar structure fabricated at the tip of the commercial Si tip using 3D-FEBID, the AFM image and measurement produced by the modified tip, emphasizing the improved resolution in imaging and lateral and depth measurement compared to the commercial tip. (b) Platinum 3D tetrapod fabricated at the tip of an AFM tip using 3D-FEBID, and an image produced through scanning thermal probe microscopy using the modified tip. (c) 3D nanoresonator of Pt-C fabricated using 3D-FIBED, and its resonance frequency response triggered by an AC electric field in a vacuum and in the presence of air, showing the shift in resonance frequency by the adsorption of air on the nanoresonator, enabling the gas sensing capability. Reproduced with permission Brown, J., Kocher, P., Ramanujan, C.S., *et al.*, 2013. Electrically conducting, ultra-sharp, high aspect-ratio probes for afm fabricated by electron-beam-induced deposition of platinum. *Ultramicroscopy* 133, 62–66. Copyright 2013 Elsevier. Sattelkow, J., Froch, J.E., Winkler, R., *et al.*, 2019. Three-dimensional nanothermistors for thermal probing. *ACS Applied Materials & Interfaces* 11 (25), 22655–22667. Arnold, G., Winkler, R., Stermitz, M., *et al.*, 2018. Tunable 3d nanoresonators for gas-sensing applications. *Advanced Functional Materials* 28 (19), 1707387.

Flat 3D Printing

Talking about 3D manufacturing, the first examples that come to mind are geometries that are more or less isotropic in a Cartesian coordinate system, but that is mainly true for purely geometrical objects. The CPU of a computer is certainly a huge and complex three-dimensional network of functional units, but while they can span over 100 square millimeters in xy direction, in the

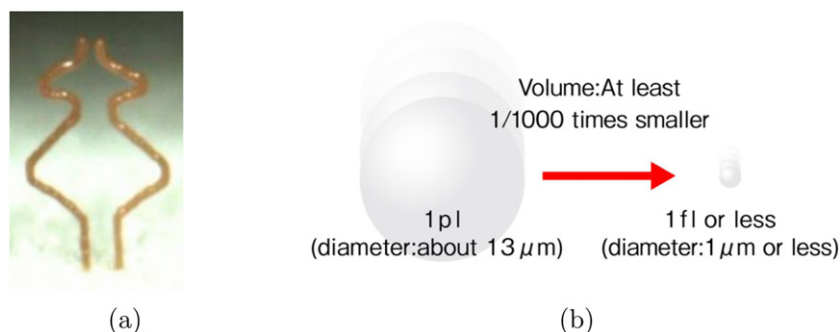


Fig. 9 (a) 1.5 mm high free-standing inkjet printed structure. The "tree" was printed by jetting an aqueous solution onto a frozen metal plate. It shows the excellent spatial and time precision that is inherited in the inkjet printing process. (b) By using the additional force created by an electric field the super inkjet technology can overcome the surface tension also for smaller droplets. The left droplets of 1 pL represent a conventional inkjet droplet while the 0.1 fL is created with super inkjet printing. Reprinted with permission from Mager, D., 2010. Microstructuring by inkjet printing Der Andere Verlag. Super inkjet technology website. URL <https://sijtechnology.com/en/>.

z-direction they only stack tens of micrometers. Nevertheless, it is simply impossible to place such functionality in a pure 2 or 2.5 D arrangement. So for many functional devices, stacking of material, with a lateral resolution much worse than the layer thickness is quite common. Besides conventional clean room technologies, there are many other technologies that create such structures at different dimensions and material mixes. Three of them are introduced here with the key benefits and drawbacks: ink-jet printing, aerosol jet printing, and laser-induced forward transfer.

Inkjet Printing

Inkjet printing or more precisely, drop-on-demand printing, includes the selective deposition of a liquid material onto a substrate without the need for a masking technology. The deposited materials are in a low-viscous form so that they can be dispensed through a small nozzle (diameter is in the range from 10 μm to a few hundred micrometers) creating droplets with a diameter similar to the nozzle. These droplets normally solidify immediately after depositing on a substrate, either via evaporating the solvent or through polymerization. Depending on the printed material, inkjet printed structures can be used for several applications, including structural mock-ups, electrical devices, and biomedical applications.

Working principle

The energy to eject a droplet can be coupled into the liquid in several ways. The most common two methods are mechanical displacement via evaporating a fraction of the ink (BubbleJet), and via acoustic energy coming from a piezoelectric actuator. This time-limited application of energy forces ink out of the nozzle. By switching off the effect after a few microseconds, the bulk of the material gets retracted, and only a small droplet ($< 100 \mu\text{m}$) is deposited from the printhead to a substrate. In the case of the thermal ink-jet process, a heater evaporates a fraction of the ink's solvent, and the resulting gas bubble expands and presses the remaining liquid ink out through the nozzle. The surrounding ink absorbs the heat from the gas bubble and causes it to collapse within a few microseconds. Mass fabrication of such heaters is fairly inexpensive, which makes this printhead economically attractive for the consumer market. One drawback is that, over time, residues from the evaporation remain on the heater, causing its performance to decay. Therefore, in this technology, printheads are typically exchanged with the ink reservoirs and discarded. Another drawback is that, for the evaporation to work reliably, the ink must have tailored properties for that purpose. The more flexible technology with respect to the ink composition, and therefore the favored method in a laboratory context, is acoustic ink-jet printing. In this technology, a mechanical actuator, mostly piezoelectric, couples an acoustic wave into the printable liquid. The system is designed in a way that the traveling wave inside the printhead focuses around the nozzle, thereby causing the ejection of a single droplet. For the ejection of larger droplets in the nanolitre range, the piezoelectric actuator simply displaces the required amount of ink mechanically (Heinzl and Hertz, 1985).

Once the liquid passes through the nozzle, the subsequent phenomenon is typically the same for all the inkjet printing mechanisms. Either by the collapse of the vapor bubble or by the retraction of the piezoelectric actuator, a negative pressure is caused in the reservoir that pulls the bulk of the ink back away from the nozzle. Only the tip of the ink column that was pressed out of the nozzle has sufficient kinetic energy to overcome the surface tension and fly away from the printhead. This whole process is highly repeatable (spatial misalignment of a few μm and volume exactly down to a few picolitres) and fast enough that the printheads can eject droplets at a kilo-hertz (kHz) rate. Fig. 9(a) shows this precision in the form of a free-standing "tree" out of frozen colored water. The 50 μm droplets froze instantly, forming a little building block on which the next droplet landed and immediately froze. This "writing in free air" is only possible since the droplets are so small that they barely have kinetic energy, and they also freeze instantly. Thereby the structure could be printed without the need for any support structures.

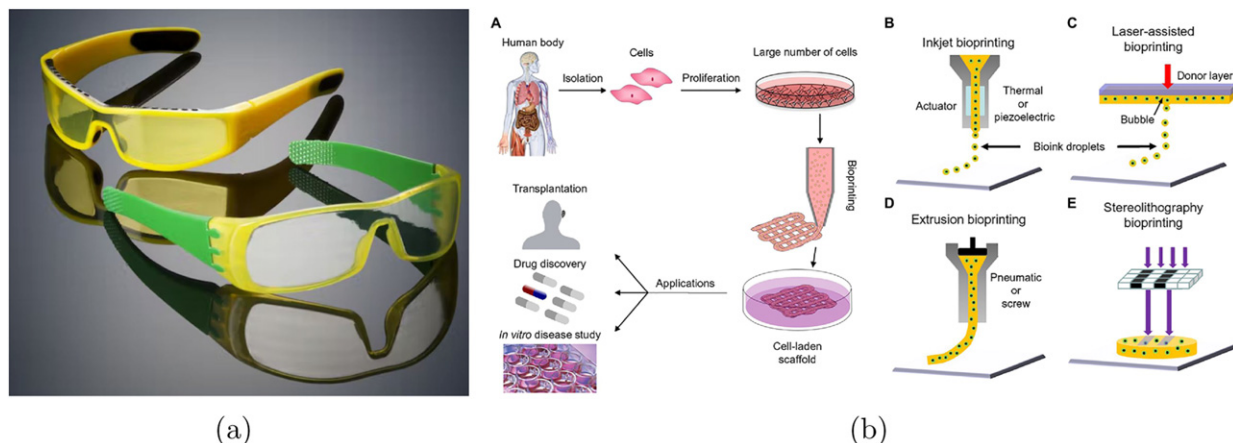


Fig. 10 (a) shows a 3D object printed with a resin inkjet printer. These photo-curable resins, are mechanically stable, allow a huge variety of colors and are even quite transparent, allowing the direct printing of something like these glasses shown her. (b) Inkjet printing can also be used for biological applications where both the scaffold as well as the cells can be deposited via inkjet printing. Often a slurry is used where the cells are embedded in the scaffold material, there the transfer can be made with inkjet printing, but also by other means. Image taken from Stratasys website - polyjet printer. URL <https://www.stratasys.com/en/>. Earnest, P.C., Toksoy, Z., Davis, B.A., Geibel. 2021. 3D bioprinting of vascularized tissues for in vitro and in vivo applications. *Frontiers in Bioengineering and Biotechnology* 9, 664188.

Since the kinetic energy needs to overcome the surface tension, there is a technical limit with respect to the minimal droplet size of around $1\text{ }\mu\text{m}$. 1 pL corresponds to a droplet with a diameter of approximately $10\text{ }\mu\text{m}$. To go below this limit, researchers at AIST (Japan) developed a technology called super inkjet printing, where they enhance the energy of the droplet by overlaying an electric field that helps the droplet to overcome the surface tension. By this trick, they can create droplets down to 0.1 fL . The droplets cannot only be smaller but the viscosity range is also much wider than in conventional inkjet printing.

Applications

The applications of structural inkjet printing are quite vast due to the broad amount of possible inks and the wide range of droplet sizes (femtolitres to microlitres). By printing colored polymerisable materials, classical 3D printing can be done (see Fig. 10(a)). By using inks based on biological materials, scaffolds for living tissue can be printed (Fig. 10(b) (Zhang *et al.*, 2012)). While the later application can have sub-micron features in form of the involved biological components, both examples are more in the micro-printing domain. This is not the case for printed electronics, where the z-direction often only reaches hundreds of nanometers. But how can one print layers that only have a few hundred micrometers thickness if they are build up using droplets that have up to tens of microns in diameter? The answer is in the composition of the ink. This liquid out of which the droplet is formed, is often a suspension, containing a solvent and the active material. A typical silver ink has 40% (wt.) silver, and the rest are solvents and stabilizers. Let's assume the density of the silver nanoparticles with 10 g/mm^3 and the solvent is water with 1 g/mm^3 , this results in a volumetric ratio of these two components of 1:15. Therefore, when the solvent evaporates from the printed structure, the remaining thickness is only one 16th of the original height, while the lateral resolution remains as before if the ink is made properly (Fig. 11).

Aerosol Jet Printing

As stated in the previous section, surface tension is the limiting factor in determining the droplet size and, thereby, the printing resolution. While additional components like the application of an electric field can help to improve the situation, getting rid of the limiting surface tension would be a beneficial approach. Aerosol jet printing follows that path by vaporizing the ink into tiny droplets ($<5\text{ }\mu\text{m}$) that are then guided onto the substrate by a carrier gas (e.g., nitrogen).

Working principle

The ink in an aerosol jet printer is not placed next to the nozzle but away from it in a reservoir. In this so-called Atomizer, the ink is vaporized into a mist of droplets with a few micron diameters. This mist now needs to be guided to the target position, which is done using a focused airflow. Therefore, the printhead has 2 main parts: a central supply line through which the material-loaded mist is fed to the nozzle and side gas outlets where a sheath flow can exit (17). This sheath flow drags along the mist and "shoots" it in a focused manner onto the substrate. This allows the direct writing of material tracks with a width of down to $10\text{ }\mu\text{m}$. Thanks to a working distance of 3–5 mm, it allows for the deposition of materials onto 3D structures (e.g., steps). The metal load of the inks used in that method is quite high so that less solvent is used, and the written tracks show fewer surface effects and can be directly sintered, to form the final structures.

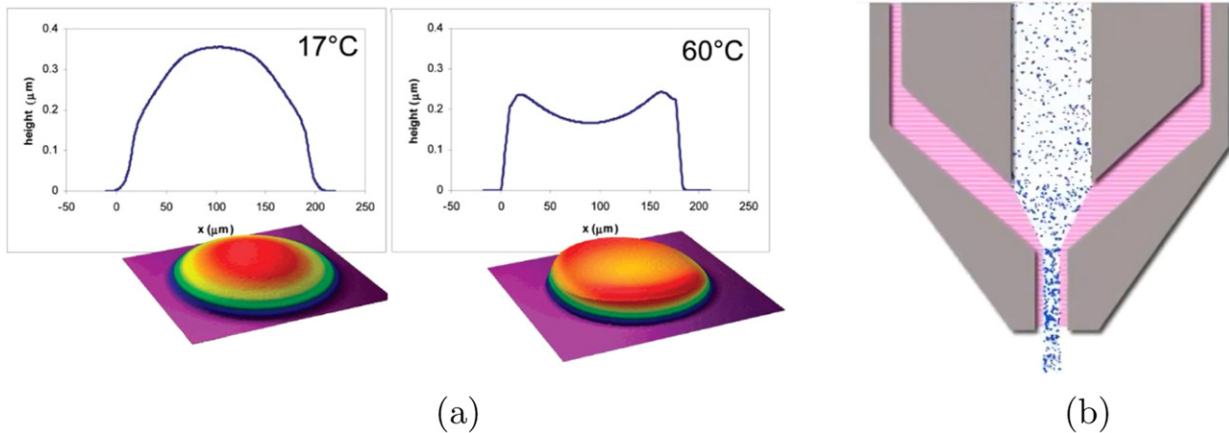


Fig. 11 (a) shows the topology of two inkjet-printed dots of PEDOT/PSS in water in dependence on the evaporation temperature. Both droplets have a diameter of 200 μm and a height of roughly 300 μm, but the top of the nanometric thickness can be tuned with temperature. (b) shows a schematic from an Aerosoljet printer the speckled area is the gas with the vaporized material, while the pink area shows the sheath gas that pushes the focused material gas to the substrate. Reproduced from Soltman, D., Subramanian, V., 2008. Inkjet-printed line morphologies and temperature control of the coffee ring effect. *Langmuir* 24 (5), 2224–2231. Available at: <https://doi.org/10.1021/la7026847>. Optomec website -. URL <https://optomec.com/printed-electronics/aerosol-jet-technology/>.

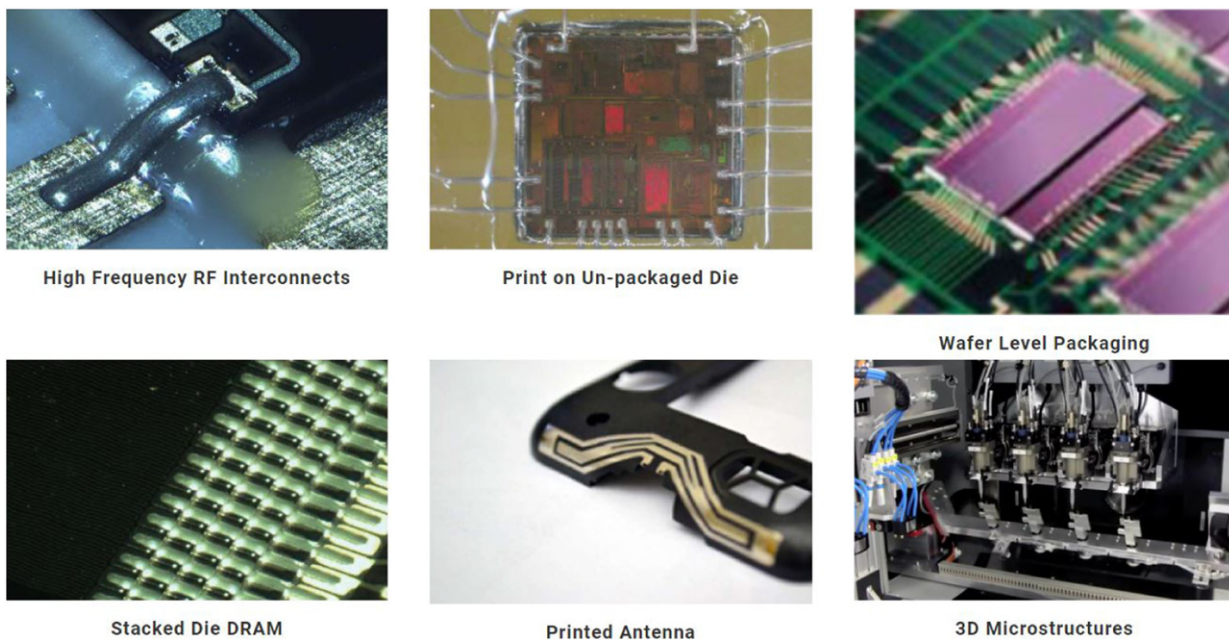


Fig. 12 These examples from the company Optomec, show the flexibility of the process when it comes to printing electrical interconnects. Aerosoljet printing is capable of printing connects of different thicknesses and also on a multitude of even non-planar substrates. Copyright Optomec. Reproduced from Optomec website -. URL <https://optomec.com/printed-electronics/aerosol-jet-technology/>.

Achievable structures

Aerosol jet printing has its benefit in the fast writing (centimetres per second) of fine structures (10 μm width). The transfer mechanism is mainly based on the kinetic energy that the sheath gas induces into the vaporized ink. This allows the writing of structures nearly independent from the substrate properties, and material on topography wise. The technology can therefore be used on a large variety of substrates and applications. **Fig. 12** shows several applications from the company Optomec a manufacturer of aerosol jet printing machines. The technology allows to directly "draw" conductive tracks onto a substrate with only a few preconditions, mainly the material must be "vapourisable" into stable droplets of a few micrometers diameter. Then this technology can deposit all types of materials, from insulators to metals and not only in a pure form but also as defined mixtures. The thickness of the deposited tracks can be varied from tens of nanometers to a few micrometers, depending on the material, printing speed or gas flow.

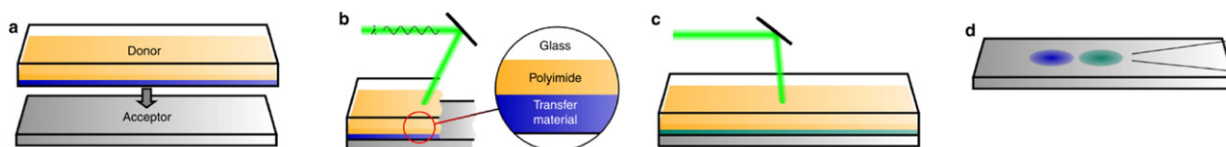


Fig. 13 LIFT is based on the spatially selective transfer of materials from different donors to acceptor slides. (a) shows an empty acceptor slide and a donor slide carrying a polyimide foil that is coated with a blue chemical. (b) locally heating the polyimide with a laser, creates bulging of the polyimide so that the blue chemical is pressed against the acceptor slide. (c) The donor is replaced with one where the polyimide is coated with a green chemical, and the laser transfer is repeated. (d) The acceptor now has little patches of blue and green chemicals without the need for masks. Taken from Loeffler, F.F., Foertsch, T.C., Popov, R., *et al.*, 2016. High-flexibility combinatorial peptide synthesis with laser-based transfer of monomers in solid matrix material. *Nature Communications* 7, 11844. Available at: <https://doi.org/10.1038/ncomms11844>.

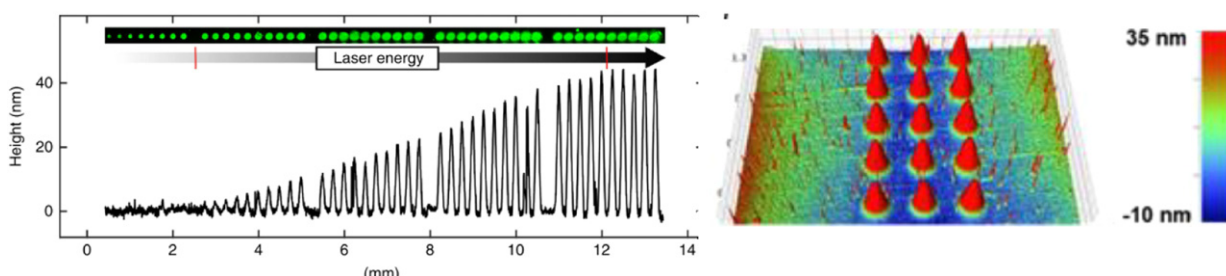


Fig. 14 A) Topography of transferred spot material in dependence of the laser energy. The height of the transferred spot material, containing an activated leucine building block, was measured with phase-shift interferometry, laser energy linearly increases from left to right in steps of 15 mJ. The range of the linear correlation of deposited material (1 nm – 50 nm) and deposited laser energy 450 mJ – 900 mJ is marked by red lines. Reproduced from Loeffler, F.F., Foertsch, T.C., Popov, R., *et al.*, 2016. High-flexibility combinatorial peptide synthesis with laser-based transfer of monomers in solid matrix material. *Nature Communications* 7, 11844. Available at: <https://doi.org/10.1038/ncomms11844>.

Laser-Induced Forward Transfer

Laser-induced forward transfer (LIFT) method allows transferring materials, that are solid or liquid at room temperature, in patches, featuring a diameter ranging from a few to hundreds of micrometers and a tunable thickness of a few nanometers to a few microns, depending on the laser parameters and the material to transfer (Constantinescu *et al.*, 2016; Visser *et al.*, 2015; Loeffler *et al.*, 2016). Due to the intrinsic alignment of the laser towards the acceptor substrate and the possibility to transfer solid materials, this makes LIFT ideal for the fabrication of arrays that contain stacks of non-identical features or material combinations (Loeffler *et al.*, 2016; Paris *et al.*, 2022).

Working principle

The idea of LIFT is to get selective depositions of nanometrically thin patches of material, without the need for a mask. The lateral resolution is typically in the range of tens to hundreds of microns (Zhang *et al.*, 2022), which is often beneficial to get a decent production speed. The basis of the technology is two glass slides, a so-called acceptor onto which the transferred material is deposited, and the donor slides that contain an evenly distributed chemical, that shall be transferred. The acceptor slide can be pre-treated before the transfer, if a surface modification (activation, ITO, catalyst, etc.) is needed but often is just an empty glass slide. The donor, on the other hand, is most of the time coated with a polyimide (Kapton) film with a thickness of around 10–50 μm . On top of this film, the chemical to be transferred is spincoated or doctorbladed with several hundreds of nanometers to a few μm thickness. The donor substrate is now placed upside down onto the acceptor slide and the sandwich is placed below a scanhead that guides a laser beam over the surface. (Fig. 13).

When the laser hits the Kapton, it expands a bit, and the chemical on top of the Kapton gets pushed down several microns and thereby pressed against the acceptor (Paris *et al.*, 2020). The Kapton and the chemical are heated up a bit by the laser while the acceptor normally remains at room temperature. In the moment of retraction (cooling of the Kapton), a thin layer of the chemical has better adhesion to the acceptor, than to the rest of the material and therefore remains on the acceptor glass. The thickness of the remaining material can be tuned via the laser parameters in a very accurate and repeatable manner (Fig. 14).

The process is highly flexible and quite efficient with respect to material consumption. Depending on the laser source and power, the laser can not only create a bubble that bulges out to then touch the acceptor and transfer material, but it can also stamp out predefined structures from the donor onto the acceptor.

Applications

The applications of the technology are quite versatile. The first publications in the 80 s used it to transfer a sub-micron thick metal layer from one slide to another (Bohandy *et al.*, 1986). Over the years, the technology was used for several materials, even for sensitive materials like bio-molecules (Serra *et al.*, 2004) or viable cells (Riester *et al.*, 2016). One quite successful application with respect to industrial relevance is the LIFT-based production of peptide arrays. Here, LIFT is used to subsequently transfer the amino acids needed to create 10–15 mer peptides (Paris *et al.*, 2022). This is a scientifically as well as commercially attractive application where the ability to selectively transfer a small amount of materials in a structured way is needed. It allows making peptide arrays on glass slides where each peptide is different from its neighbors. So for thousands of different peptides on one microscope slide, one only needs to place 15–20 different donor slides into the system and transfer the corresponding amino acid onto each spot. After a coupling and chemical washing step, the next amino acids are transferred and coupled. Thus, for a 10-mer peptide, this needs to be repeated 10 times. The technology is quite versatile as a deposition tool for nanometric material layers. Therefore, it will quite likely be applied to many more fields in the future.

Conclusions and Outlook

3D nanoprining has enormous potential for research and development, and, thereby, societal life. At its infant stage, this field has been showing phenomenal promise to that through the fabrication of diverse and complex 3D architectures that could not be done before at these length-scales, exhibiting novel and superior functionalities compared to the existing macroscopic 3D printed structures, and a vast portfolio of proof-of-concept applications. However, the current methodologies also feature several challenges. For example, even though 2PP and FEBID allow complex 3D architectures with high control and nanoscale features, they are fairly slow and highly expensive, which limits their applicability and transformation into large-scale manufacturing. On the other hand, inkjet printing and aerosol jet printing are limited to 2.5D structures. Few other 3D printing technologies, such as electrohydrodynamic printing and single photon lithography still can not reach a sub-micrometric resolution. Transforming these into "true" 3D nanoprining platform requires further extensive technological development. However, these challenges shape the future directions of the field of 3D nanoprining. With novel innovations in nanotechnology and micro/nano-manufacturing, 3D nanoprining can further shape the fields, ranging from electronics to healthcare to space explorations.

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Materials for Biocompatible Piezoelectric Devices

Meysam T Chorsi, Thanh T Le, Ritopa Das, and Tra Vinikoor, University of Connecticut, CT, United States

Hamid T Chorsi, University of California Santa Barbara, Santa Barbara, CA, United States

Kazem Kazerounian, Horea Ilies, and Thanh D Nguyen, University of Connecticut, CT, United States

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Abstract

Advances in materials, engineering, and biotechnology have opened up exciting research directions in the areas of biosensors and bioactuators. An exciting and promising direction is to construct biodevices based on biocompatible piezoelectric materials. These biodevices present distinctive, innovative, and safe integrating approaches with biological systems for applications in sensing biological forces, stimulating tissue growth and healing, and diagnosing medical problems, to name a few. In this chapter, we present a general overview of the fundamentals, applications, and the future opportunities as well as challenges of biocompatible piezoelectric materials. Piezoelectric biosensors and actuators are developed with advanced methods in microfabrication and materials-processing to avoid any toxicity from conventional piezoelectric materials. Interestingly, several piezoelectric materials are biodegradable in nature, which eliminates the need for invasive implant extraction. We will also review them in this chapter. Advancements in the field of piezoelectric biomaterials integrated with microsystems hold great promises for biomedical applications.

Introduction

Biomaterials are a category of natural, synthetic, alive or lifeless materials which can safely interact with biological systems to perform or substitute a natural function (Biomaterials, 2021). These materials should be non-toxic, non-injurious and non-immunogenic, i.e., being biocompatible, to be used in a variety of applications involving tissue engineering, (Hutmacher, 2000; Kim and Mooney, 1998; Temenoff and Mikos, 2000) minimally invasive sensors, (Yu *et al.*, 2006; Chen *et al.*, 2010; Daddona *et al.*, 2000) drug delivery devices (Park and Park, 1996; Voskerician *et al.*, 2003; Vallet-Regí *et al.*, 2007) etc.

Piezoelectric materials are a class of both organic (mostly polymers) and inorganic materials that can transform mechanical force into electricity and vice versa. In inorganic piezoelectric crystals, piezoelectricity happens as a result of the arrangement of ions in the non-inverse symmetric structure of the dielectric material (Ramadan *et al.*, 2014). Developed electrical field across the material boundary is caused by the internal polarization of the material and is linearly related to the applied stress. In organic piezoelectric polymers, piezoelectric effect is produced by the molecular assembly of the polymer and its orientation (Ramadan *et al.*, 2014; Harrison and Ounaies, 2002). Piezoelectricity can also be found in several mammalian tissues. For example, hair, wool, horns and hooves are commonly composed of α -Keratin with a closely ranged and polarized α -helical structure. Additionally, most parts of the musculoskeletal tissue have a collagenous structure. Collagen has a spiral arrangement with three helical fibrils. Each collagen fibril exhibits lateral piezo response along the fibril axis, making collagen a piezoelectric material which imparts this property to all the tissues that it composes. Thus bones, cartilage, ligaments and tendons are all piezoelectric in nature (Rajabi *et al.*, 2015; Ribeiro *et al.*, 2015).

Applications of piezoelectric technologies for applications in biological systems represent a thrilling area of rapid development. It is feasible for inorganic piezoelectric materials to be biocompatible or can be biocompatible after being encapsulated. More well-known of them are PZT (lead zirconate titanate), (Qi *et al.*, 2012) AlN (aluminium nitride), (Nathan *et al.*, 2013) ZnO (zinc oxide), (Dagdeviren *et al.*, 2013) BaTiO₃ (barium titanate), (Jeong *et al.*, 2013) LiNbO₃ (lithium niobate), (Wang *et al.*, 2014a) and quartz (Wilson *et al.*, 1981). Most of organic materials are biocompatible and environmentally welcoming in nature. Polar polymers, such as PVDF (polyvinylidene fluoride), are ferroelectric and display tensile piezoelectric effects after poling treatments (Asaka and Okuzaki, 2014). Optically active polymers such as PLLA (poly(L-lactic acid)) and PDLA (poly(D-lactic acid)), demonstrate shear piezoelectric effects after uniaxial elongation (Yoshida *et al.*, 2014; Fukada, 1995). Two clear advantages of piezoelectric polymer based devices are that they are typically less expensive in terms of material cost and processing technology and do not generally demand advanced microfabrication facilities (Ramadan *et al.*, 2014). However, the down side is that compared to inorganic piezoelectric materials, an organic piezoelectric material commonly does not have a analogous piezoelectric output (Ohnuma, 2013).

Biocompatible piezoelectric materials when crafted into small structures, become a powerful instrument which can be interfaced with biological tissues and exploited for miniaturized bioelectronic and biomechanical devices. In this regard, piezoelectric materials perform a significant function in the field of biomedical microelectromechanical systems (BioMEMS).

Here, we deliver a detailed and systematic review of various piezoelectric biomaterials that can be used in the field of BioMEMS. The focus of the chapter will be on the functioning principles, properties and biomedical applications. Among general piezoelectric materials utilized in the development of BioMEMS such as PVDF, PZT, ZnO, AlN, and PLLA, emphasis will be given to the organic piezoelectric materials which can find admirable uses, particularly for medical sensors. To be comprehensive, thorough analysis between several organic piezoelectric materials and their most common inorganic counterparts for BioMEMS applications is also offered. The chapter is concluded with remarks on the future trends and challenges of piezoelectric biomaterials for biomedical applications.

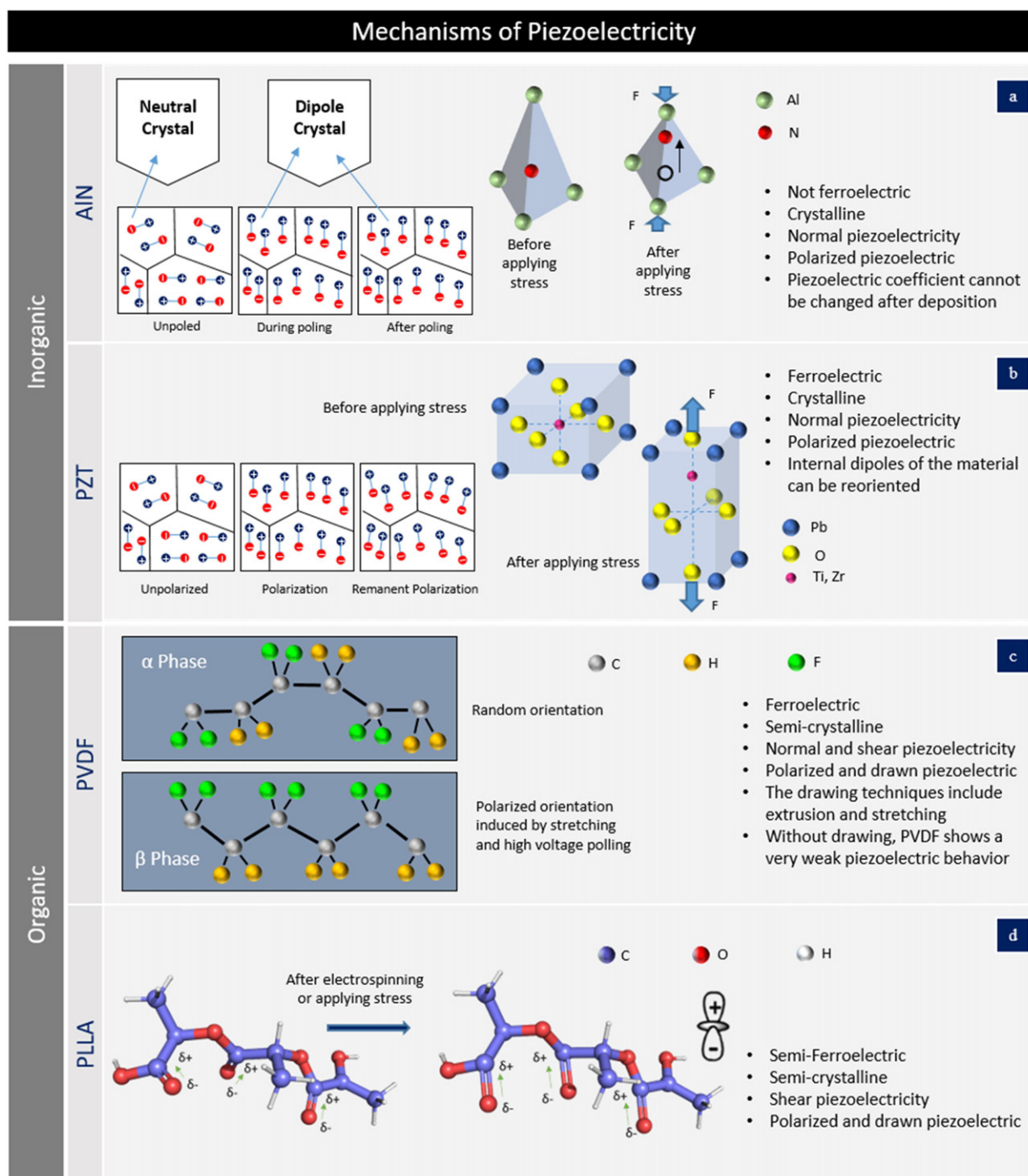


Fig. 1 Mechanisms of piezoelectricity in different materials. (a) polarization process of AlN and the effect of piezoelectricity on the tetrahedral coordinate of a AlN crystal (b) polarization process of PZT and stress-induced phase transition in PZT (c) Structures of non-piezoelectric (α -phase) and piezoelectric (β -phase) PVDF (d) Molecular structure of PLLA chain with orientation of C=O dipoles in all directions and preferential orientation of the C=O dipoles after electrospinning process. Reproduced from Trolier-McKinstry, S. and P. Murali, 2004. Thin film piezoelectrics for MEMS. *Journal of Electroceramics* 12(1), 7–17. Priya, S., *et al.*, 2017. A review on piezoelectric energy harvesting: materials, methods, and circuits. *Energy Harvesting and Systems* 4 (1), 3–39. Qi, Y., *et al.*, 2012. Stretchable piezoelectric nanoribbons for biocompatible energy harvesting. *Stretchable Electronics* 111–139. Li, Q. and Q. Wang, 2016. Ferroelectric polymers and their energy-related applications. *Macromolecular Chemistry and Physics* 217 (11), 1228–1244. Sultana, A., *et al.*, 2017. Human skin interactive self-powered wearable piezoelectric bio-e-skin by electrospun poly-l-lactic acid nanofibers for non-invasive physiological signal monitoring. *Journal of Materials Chemistry B* 5(35), 7352–7359.

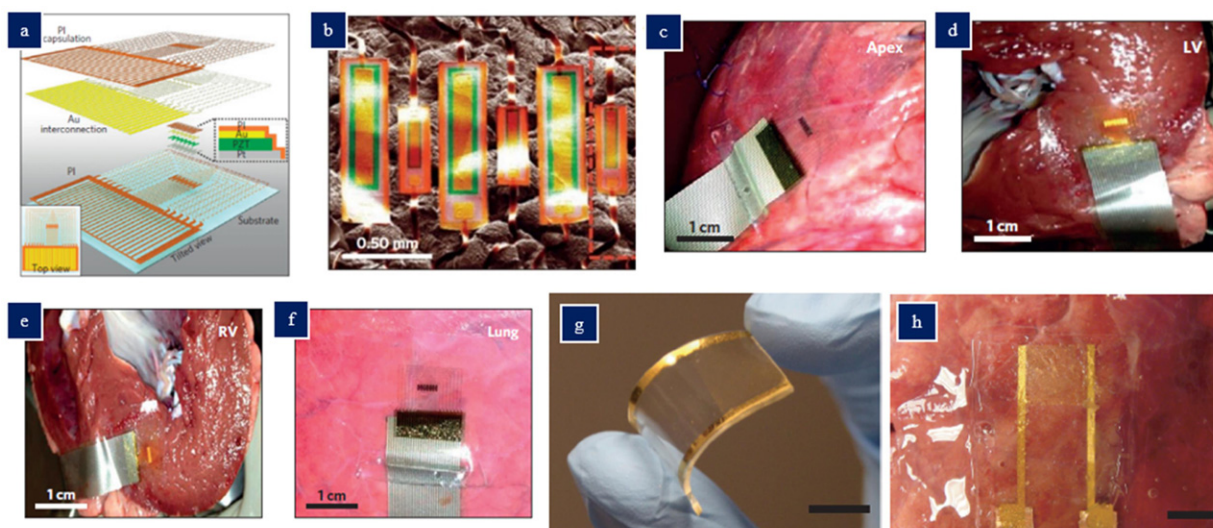


Fig. 2 Applications of inorganic piezoelectric materials. (a-f): Compliant modulus sensor (CMS) based on nanoribbons of PZT in arrays of mechanical actuators and sensors. (a) Exploded-view schematic illustration of the device, with a top view in the lower-left inset, and a cross-sectional view of actuators and sensors in the black dashed line. (b) SEM image of a device on an artificial skin sample (c-f) Photographs of a device placed on: (c) heart apex (d) left ventricle (e) right ventricle (f) lung. (g,h): Piezoelectric nanoribbons for monitoring cellular deformations (g) Photograph of flexible PZT nanoribbon chip (h) Photograph of PZT nanoribbons on PDMS biointerfaced with cow lung tissue for sensing deformations during a mimicked respiration process. Reproduced from Dagdeviren, C., *et al.*, 2015. Conformal piezoelectric systems for clinical and experimental characterization of soft tissue biomechanics. *Nature Materials* 14(7), 728–736. Nguyen, T.D., *et al.*, 2012. Piezoelectric nanoribbons for monitoring cellular deformations. *Nature Nanotechnology* 7(9), 587–593.

Mechanisms of Piezoelectricity in Inorganic and Organic Materials

From microscopic perspective, dislocation of ions inside crystals produces piezoelectricity in inorganic material. Induced changes in the atomic structure of the crystal under external stress shift the balance of ions in the structure which creates a dipole moment. For a net polarization to happen, the induced dipole must not be cancelled out by the other dipoles in the unit cell. For this to happen, the piezoelectric atomic structure must be non-centrosymmetric, i.e., there must be no center of symmetry. **Fig. 1** represents the piezoelectricity process (polarization development) for various materials. For AlN as a tetrahedrally bonded semiconductor, there is a N atom in a tetrahedral interstice enclosed by four Al atoms (**Fig. 1(a)**) (Fu *et al.*, 2017). In each interstice, there is no center of symmetry, so when an external stress is directed, the motion of the central atom produces a dipole moment (Que *et al.*, 2016). The polarization process for PZT is analogous to AlN. PZT is a non-centrosymmetric crystal structure (**Fig. 1(b)**) and has a net non-zero charge in each unit cell of the crystal before applying mechanical stress. After the application of stress, there is a disposition in the site of the titanium ion inside the unit cell, as a consequence, electrical polarity is obtained. Finally, the unit cell turns into an electric dipole (Qi *et al.*, 2012). For inorganic materials like AlN and PZT, piezoelectricity is produced by poling the material under a high electric field at an elevated temperature. Piezoelectric coefficient in AlN thin film is extremely dependent on the crystal orientation of the film, which ordinarily cannot be altered after deposition. In contrast, in PZT a remnant polarization at zero applied electric field is endured due to the reorientation of the internal dipoles of the material under the application of an external electric field (Ramadan *et al.*, 2014).

In organic materials, on the other hand, piezoelectricity is the process of reorienting the molecular dipoles within the bulk polymer. This can be accomplished through the application of a high electrical field or stretching (drawing). **Fig. 1(c)** depicts this process for PVDF. Five crystal phases (α , β , γ , δ , ϵ) have been reported for PVDF, and α and β phases are the most common (Li and Wang, 2016). The α phase results in non-polar crystal structures as a results of the chains being packed in the unit cell and that the molecular dipoles are anti-parallel. The β phase is the one that displays outstanding piezoelectric properties. In this phase, all the dipoles are parallel and contribute to the highest dipolar moment per unit cell (Wan and Bowen, 2017). **Fig. 1(d)** (left) displays PLLA in the α -crystalline form (thermodynamically stable conformation), where the C=O dipoles are randomly oriented along the main chain. In order to induce piezoelectricity, the chains must be thermally stretched to convert the α -crystalline form into β -crystalline form, which represents a change from randomly oriented molecular chains to molecular chains being aligned along the stretched direction (Sultana *et al.*, 2017). Electrospinning process can also align the C=O bond to create piezoelectric PLLAs as seen in **Fig. 1(d)** (right).

Device Application From Different Piezoelectric Materials

Applications of Inorganic Piezoelectric Materials

PZT sensors

$\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$ (PZT) with a crystalline, perovskite structure is widely used in piezoelectric devices. PZT is a metallic oxide based ceramic piezoelectric material acquired by scientists at the Tokyo Institute of Technology around 1952 (Bao, 2014). In comparison to previously determined metallic oxide based piezoelectric materials, PZT demonstrates superior sensitivity and has a higher operating temperature. Furthermore, PZT is materially strong, chemically inert and rather inexpensive to manufacture (Swallow *et al.*, 2008; Paul and Roy, 2015). Additionally, it can be readily tailored to meet the requirements of a particular purpose. Owing to its large piezoelectric charge constant, PZT acquires excellent electromechanical properties, rendering it exceptionally attractive for applications in BioMEMS devices (Cung *et al.*, 2013). Although PZT and inorganic materials in general possess mediocre flexibility and elasticity when compared with their organic counterparts, several inorganic materials with ultrathin films or nanowires (NWs) can exhibit good mechanical flexibility (Zang *et al.*, 2015). Recently, ultrathin films or NWs of PZT have also been extensively examined for flexible and stretchable pressure sensing devices (Bao *et al.*, 2015; Pan *et al.*, 2013).

Biocompatibility is essential for the application of BioMEMS sensors *in vivo* or *in vitro*. Biocompatibility has been investigated for PZT, which contains lead. Lead is known to adversely influence organisms (Jaishankar *et al.*, 2014). Several research groups have attempted to synthesize a biocompatible piezoelectric ceramic material. They attempted to prevent spoiling piezoelectric properties by coating the PZT surface with titanium which has a high biocompatibility and has been widely used in orthopedic metallic implants (Sakai *et al.*, 2006; Morita, 2010; Cernea *et al.*, 2010).

PZT based BioMEMS sensors have been used in many biomedical applications including sensing and powering for *in vivo* experiments (Dagdeviren *et al.*, 2014; Yuan, 2016; Dagdeviren *et al.*, 2015; Nguyen *et al.*, 2012; Park *et al.*, 2017). In a notable and a pioneering work, PZT nanoribbons developed by Dagdeviren *et al.* (2015) were used for *in vivo* measurements of soft tissue viscoelasticity (Fig. 2(a-f)). The device was realized using stacking and micro-contact transferring method (Fig. 2(a)). An array of actuators was bonded to the skin and stimulated to produce tissue deformations which can be measured by another set of the PZT sensors to deliver information on mechanical properties of the skin (Fig. 2(b)). Compared to the invasive conventional characterization methods which are mostly tailored only for a particular region of the body, their realized structure attained conformal contact with the underlying complex texture of the targeted skin. The authors validated their piezoelectric actuator-sensor system by applying them on a range of soft biological tissues and organ systems in animal models. Fig. 2(c-f) shows the *ex vivo* measurements from the apex of the bovine heart, left (LV) and right (RV) ventricle, and lung. The clinical significance of these devices for rapid and non-invasive characterization of skin mechanical properties has been established on human subjects.

In an interesting work, Nguyen *et al.* (2012) used PZT nanoribbons to measure mechanical deformations of cell and tissue deformation. They transferred arrays of PZT nanoribbons onto a silicone elastomer and measured mechanical deformations of an explanted cow lung during a simulated respiration (Fig. 2(g,h)). The PZT nanoribbons offer a minimally invasive and scalable stage for electromechanical biosensing. Nevertheless, works to examine long-term biocompatibility of the PZT nanoribbons *in vivo* should be performed prior to the use of these PZT-based devices in the human body.

AlN sensors

AlN as a piezoelectric material has been commonly utilized in the fabrication of high frequency resonators, filters, sensors, optical devices, acousto-optic devices, surface acoustic wave (SAW) devices and bulk acoustic wave (BAW) devices. Earlier work with high quality AlN substrates was investigated in the early 1990s (Subramani and Devarajan, 2014). The stability of AlN products and the processing technologies have been developed considerably to the point that AlN-based devices are today in use worldwide. The nontoxic AlN continues to be one of the most attractive materials for BioMEMS applications due to several appealing properties, such as chemical stability, being a wide-bandgap, and high acoustic velocity. Ultrahigh acoustic velocity and good electromechanical coupling ability, (Shih *et al.*, 2014) make AlN thin films very demanding for gigahertz devices. Besides, AlN is a very promising piezoelectric material for sensing applications. AlN piezoelectric acoustic biosensors offer real-time responses and quantified data. Some specific biomolecules and proteins can be sensed through AlN biosensors (Cannatà *et al.*, 2012; Chen *et al.*, 2013). Chen *et al.* (2013) reported a highly sensitive AlN biosensor for pesticide residue detection. In their work, acetylcholinesterase enzyme is attached as the sensitive coating on one of the faces of the piezoelectric resonator. The traces of organophosphorus pesticides in the solution were detected from the reduction of the frequency shift compared with the levels found in their absence. The AlN biosensor exhibits an outstandingly low detection limit, a linear response, and good reproducibility. Their proposed method can be extended to sense a variety of biological reactions, such as antigen-antibody binding, protein-ligand interactions and genetic hybridizing, which can deliver information for the studies of biological reaction kinetics. AlN is widely utilized for acoustic biomedical devices (Wingqvist *et al.*, 2005; Mahdavi *et al.*, 2014; Iqbal *et al.*, 2014; Voiculescu and Nordin, 2012; Wingqvist *et al.*, 2007) because of its high acoustic velocity (the highest among all piezoelectric materials), relatively high piezoelectric coefficient and CMOS compatibility (Lin *et al.*, 2010a; Benetti *et al.*, 2005). It has been shown that AlN can maintain its piezoelectric properties at high temperatures as well (Lin *et al.*, 2010b).

Other inorganic piezoelectric sensors

A variety of inorganic piezoelectric materials are used in MEMS pressure sensors, but their application is generally limited to some specific areas. Here we will briefly mention quartz, ZnO, GaN, and other perovskite materials.

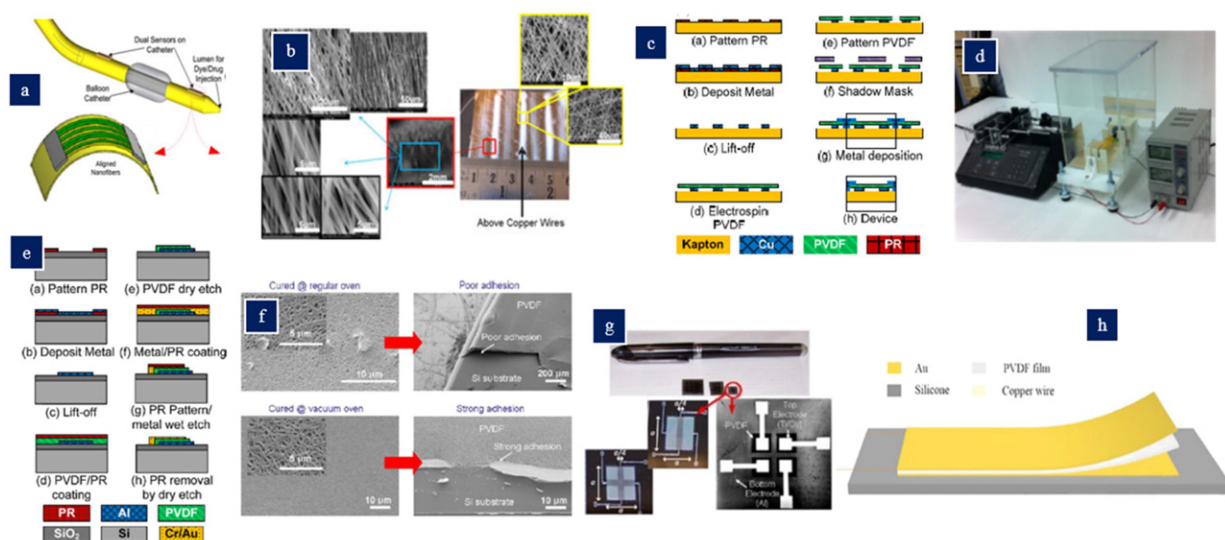


Fig. 3 Applications of PVDF-based sensors. (a-d): (a) Smart catheters with nanofiber-based pressure sensors. (b) Photograph and SEM images showing patterned nanofibers in aligned and random orientations. (c) Schematic for fabrication of electrospun nanofiber based devices (d) Photograph showing the electrospinning setup for fabricating highly aligned fibers with rotating drum as the ground collector electrodes. (e-g): (e) Fabrication process for PVDF-TrFE devices. (f) SEM images of PVDF-TrFE thin film on substrate (g) Fabricated metal-PVDF-TrFE-metal (MIM) structured pressure sensors of dual and quadruple membrane devices (bottom half) showing the device dimensions. (h): Structure of the wearable PVDF electrospun sensor for health monitoring. Reproduced from Sharma, T., *et al.*, 2013b. Aligned electrospun PVDF-TrFE nanofibers for flexible pressure sensors on catheter. In: Proceedings of the Solid-State Sensors, Actuators and Microsystems (TRANSDUCERS & EUROSENSORS XXVII). IEEE. Sharma, T., *et al.*, 2012. Patterning piezoelectric thin film PVDF-TrFE based pressure sensor for catheter application. Sensors and Actuators A: physical 177, 87–92. Liu, Z., *et al.*, 2017. Flexible piezoelectric nanogenerator in wearable self-powered active sensor for respiration and healthcare monitoring. Semiconductor Science and Technology 32(6), 064004.

It has been shown that quartz crystals can generate piezoelectric response under applied AC voltage. For example, quartz mass sensors, known as quartz crystal microbalances (QCM) can detect mass variations due to molecular interactions on the surface of the sensor (Li *et al.*, 2011). When the bioreceptor binds to the surface, the crystal can then be removed with buffer before the addition of the viral target in suspension, which adds to the mass and decreases the frequency (Caygill *et al.*, 2010). Furthermore, QCM devices can detect rapid, real-time responses to binding events on the crystal surface, and due to this they have been regularly applied to biodetection applications (Hewa *et al.*, 2009; Chen *et al.*, 2011; Jaramillo *et al.*, 2014; Sangeetha and Juliet, 2014; Yuan and Han, 2015). One major limitation of QCM devices is nonspecific adsorption of molecules existing in real matrices. This is mainly a result of potential interference from surrounding molecules that bind or adsorb on the surface (Yurish, 2014).

Zinc oxide (ZnO) is an inorganic piezoelectric material with remarkable properties such as excellent transparency, (Wei, 2009) high electron mobility, (Janotti and Van, 2009) and biocompatibility (Zhang *et al.*, 2013). ZnO can be used for flexible mechanical energy harvesting and as an active material for transient electronics and strain sensing devices (Chu *et al.*, 2013; Lu *et al.*, 2014). Most ZnO applications are focused on film bulk acoustic resonators (FBARs) and surface acoustic wave (SAW) sensors. Another property of ZnO is that it dissolves in biofluids (Dagdeviren *et al.*, 2016). We should point out that although ZnO possesses many great advantages, but its high temperature during fabrication process (usually between 400 and 500°C) (Kumar *et al.*, 2015) limits its application to some specific areas.

Besides PZT, some other perovskite piezoelectric materials such as BaTiO₃ (barium titanate), CaTiO₃ (calcium titanate), LiNbO₃ (lithium niobate), MgSiO₃ (enstatite), PMN-PT (lead magnesium niobate-lead titanate), and BZT-BCT (barium zirconate titanate-barium calcium titanate) are also exploited in BioMEMS. These materials are becoming more popular mainly because of global restrictions on PZT-based piezoelectric materials due to the Pb toxicity. Thus, there is an urgent need to develop a non-Pb substitute that can compete with PZT. However, non-Pb piezoelectric ceramics commonly have inferior piezoelectricity compared to PZT (Liu and Ren, 2009). Recently perovskite piezoelectric materials such as BaTiO₃ are getting more appealing due to their higher piezoelectric constants (Saravanakumar *et al.*, 2014). BaTiO₃ could have better performance than ZnO as a power source, but ZnO could be the best choice as a voltage source (Bystrov *et al.*, 2012).

Gallium nitride (GaN), as a III-V semiconductor, is a biocompatible piezoelectric material (Jewett *et al.*, 2012). Additional advantages of GaN include a large energy bandgap of 3.4 eV, (Jung, 2002) high electron mobility, (Meneghesso *et al.*, 2008) excellent chemical stability (Guo *et al.*, 1996) and low electrical drift of GaN biosensors in ionic solutions (Gupta *et al.*, 2008). It has been shown that gallium nitride keeps no bio-functional impact on cellular environments, (Hofstetter *et al.*, 2012) which is an important parameter for future biosensing applications.

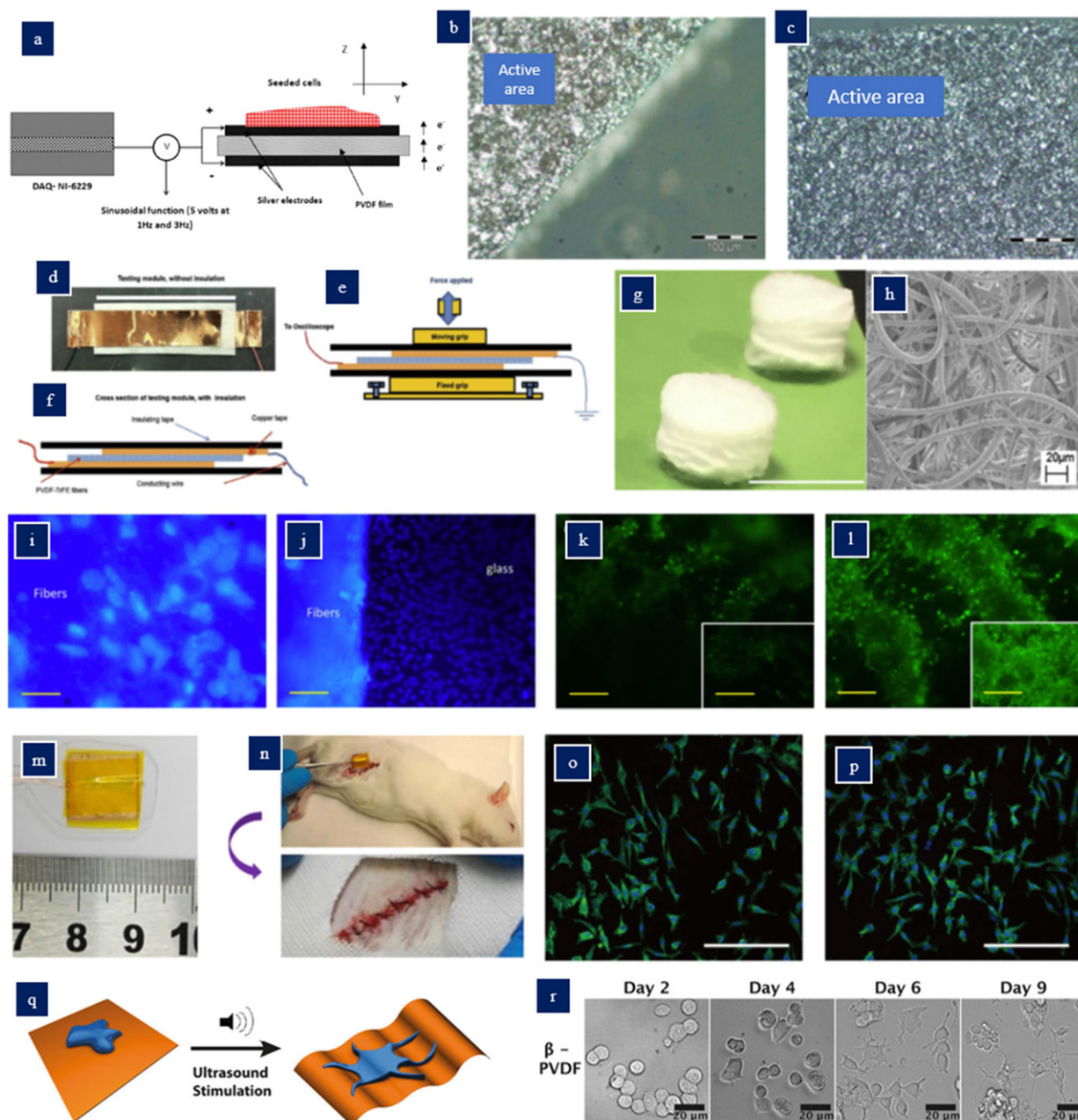


Fig. 4 PVDF-based actuators and tissue stimulators (a-c): (a) This scheme illustrated the cell culture exposition to micro vibration when seed in the active area of the piezoelectric substrate (b), (c) Images in optical microscope that shows the distribution of the PMMA/Bonelike in the PVDF membrane. (d-h): (d) Top-down view of the electrical testing setup where the piezoelectric material is sandwiched between copper tape (e) Side-view (f) Schematic of the testing device where force is applied and recording made by the oscilloscope (g) SEM images of as-spun PVDF-TrFE (h) Annealed PVDF-TrFE. (i-l): Panel showing in vitro interaction of cells with BTNP/PVDF under fluorescence microscopy (i) Micrograph showing cell nuclei in the fibers (j) Micrograph displaying many cell nuclei on the glass around the fibers (k) Conventional culture (static culture), and (l) Bioreactor culture (dynamic culture). (m-p): (m) Image of electrospun PVDF-TrFE nanofiber scaffolds before implantation (n) The demonstration process of implanting the actuator in the subcutaneous thigh region of a Sprague Dawley (SD) rat (upper right) and the implanting site after suturing (lower right) (o) Fluorescence microscopy images of L929 fibroblast cells on excited unpoled PVDF-TrFE and (p) excited poled PVDF-TrFE scaffolds after 3 days. (q-r): (q) Ultrasound (US) stimulation of the piezoelectric β -PVDF membrane induces neuronal differentiation of PC12 cells due to wireless, mechanical deformation of the β -PVDF membrane (r) Time-lapse images of PC12 cells stimulated by piezoelectric β -PVDF upon US stimulation. Reproduced from Frias, C., *et al.*, 2010a. Piezoelectric actuator: Searching inspiration in nature for osteoblast stimulation. *Composites Science and Technology* 70(13), 1920–1925. Damaraju, S.M., *et al.*, 2017. Three-dimensional piezoelectric fibrous scaffolds selectively promote mesenchymal stem cell differentiation. *Biomaterials* 149, 51–62. Mota, C., *et al.*, 2017. Design, fabrication and characterization of composite piezoelectric ultrafine fibers for cochlear stimulation. *Materials & Design* 122, 206–219. Hoop, M., *et al.*, 2017. Ultrasound-mediated piezoelectric differentiation of neuron-like PC12 cells on PVDF membranes. *Scientific Reports* 7(1), 4028.

Applications of Organic Piezoelectric Materials

PVDF biodevices

Polyvinylidene fluoride (PVDF) and its copolymer Poly-vinylidene fluoride-Trifluoroethylene (PVDF-TrFE) are popular flexible organic piezoelectric materials (Dagdeviren *et al.*, 2016). Piezoelectricity properties of PVDF was discovered in 1969 (Marutake, 1995). PVDF and its copolymers, such as PVDF-TeFE (Poly-vinylidene fluoride-Tetrafluoroethylene) and PVDF-TrFE are considered anisotropic materials (Kochervinskii, 2003). Unlike other popular piezoelectric materials, such as PZT, PVDF has a negative d_{33} value. Physically, this means that PVDF will compress when exposed to the same electric field that makes PZT expand (Uchino, 2012). PVDF as a piezoelectric polymer is widely used in the medical industry and has been extensively studied by various researchers worldwide. The inertness of PVDF makes it a noble candidate for use in surgical meshes and sutures while its piezoelectricity makes it an appropriate material for wound healing (Guo *et al.*, 2012). It is very challenging to find pure PVDF film that is used as a packaging film in biomedical devices due to some disadvantages such as its inability to form smooth films and poor adhesion to other materials (Teo *et al.*, 2016; Qin *et al.*, 2014). Endeavors have been made to use PVDF together with other materials to form composites that would overcome such drawbacks (Fadhil *et al.*, 2014; Dang *et al.*, 2003; Kono *et al.*, 2012). Recent developments in the use of PVDF have shown diverse applications for this material. Below we discuss some of them.

A. Sensors

PVDF-TrFE is a flexible material with suitable biocompatibility for biosensing (Zang *et al.*, 2015). PVDF-TrFE thin films can operate as active elements in pressure sensors with fast recovery times and a wide operating pressure range, suggesting potential applications in flow sensing for *in vivo* biomedical applications (Hartono *et al.*, 2013; Ke *et al.*, 2017).

PVDF originally found its use as a pressure sensing element in endovascular catheters (Li *et al.*, 2010; Sharma *et al.*, 2012, 2013a; Li *et al.*, 2008; Sharma *et al.*, 2013b). In a notable example, PVDF-TrFE nanofibers have been utilized to detect the pressure in catheters (Sharma *et al.*, 2013b, 2015). In this work, core-shell nanofibers are fabricated using PEDOT (conductive polymer) as a core and comprising PVDF-TrFE as a shell (Fig. 3(a)). A thin film of copper is deposited to form the external electrode. Subsequently, highly aligned nanofibers were fabricated to considerably boost device sensitivity and flexibility (Fig. 3(b)). Fabrication procedure of electrospun nanofiber-based sensor and electrospinning setup are presented in Fig. 3(c, d). Flexible core-shell-based nanofibers have shown great promise for the realizations of more robust, reliable, flexible pressure sensors on catheters to revolutionize the field of minimally invasive surgeries.

PVDF pressure sensors have been used by Sharma *et al.* (2012) to measure the real time flow in catheter applications. This is accomplished by spin-coating PVDF-TrFE copolymer into thin films to tap the near β -phase formation. The biocompatible PVDF-TrFE pressure sensor is fabricated using low-cost, low-temperature standard lithography techniques (Fig. 3(e)), and later integrated with a catheter for intravascular measurements. This process is fully compatible with existing micromachining fabrication processes without additional mechanical stretching and electrical poling. Different ratios of PVDF-TrFE and curing processes are studied by researchers to find the optimum conditions for better adhesion (Fig. 3(f)). They found that the surface with patterned electrode only contributes towards the output signal rather than the PVDF area. As a result of its fast recovery time (0.17 s), biocompatibility, and compact form factor, this sensor (Fig. 3(g)) revealed great potential for pressure and flow direction measurements as implantable biomedical devices.

In another work, a wearable self-powered PVDF sensor is fabricated by Liu *et al.* (2017) for respiration sensing and healthcare monitoring. The structure of the piezoelectric sensor is illustrated in Fig. 3(h). Both surfaces of the compressed PVDF film are compactly sandwiched by gold electrodes while a silicone substrate is used to enhance the flexibility of the whole device. The sensor has been implanted in different parts of the body for different applications. It can be used as a physiological signal recording system to measure respiration signals, or as a detector to detect human gestures and vocal cord vibrations. Since the piezoelectric sensor can sense very delicate muscle movements, it has promising applications in paralysis recovery of stroke patients.

B. Actuators and Tissue stimulators

Several studies have shown that biocompatible piezoelectric actuators like PVDF actuators can be used for tissue engineering scaffolds to promote tissue regeneration.

Frias *et al.* (2010a, b) used a PVDF actuator to experimentally confirm the use of piezoelectric materials as a means of directly straining bone cells by converse piezoelectric effect. The actuator comprises of a thin film of PVDF, printed with silver ink on both sides as electrodes (Fig. 4(a)). To improve adhesion of osteoblasts to the device surface, the PVDF surface is coated with PMMA/Bonelike (Fig. 4(b, c)). Later, osteoblasts were grown on the surface of the piezoelectric material and cellular response was studied. These results indicate that both static and dynamic substrates affect cell viability and proliferation.

Damaraju *et al.* (2017) showed that piezoelectric materials can be fabricated into flexible, three-dimensional fibrous scaffolds and can be used to stimulate human mesenchymal stem cell differentiation. Fig. 4(d-f) shows the testing setup and the device used to measure the electrical output from the bulk scaffold. The electrospun piezoelectric scaffolds and the annealed PVDF-TrFE fibers are illustrated in Fig. 4(g) and Fig. 4(h), respectively. The realized piezoelectric scaffolds with a high output voltage facilitated osteogenic differentiation. On the other hand, the scaffolds with a low voltage output assisted chondrogenic differentiation.

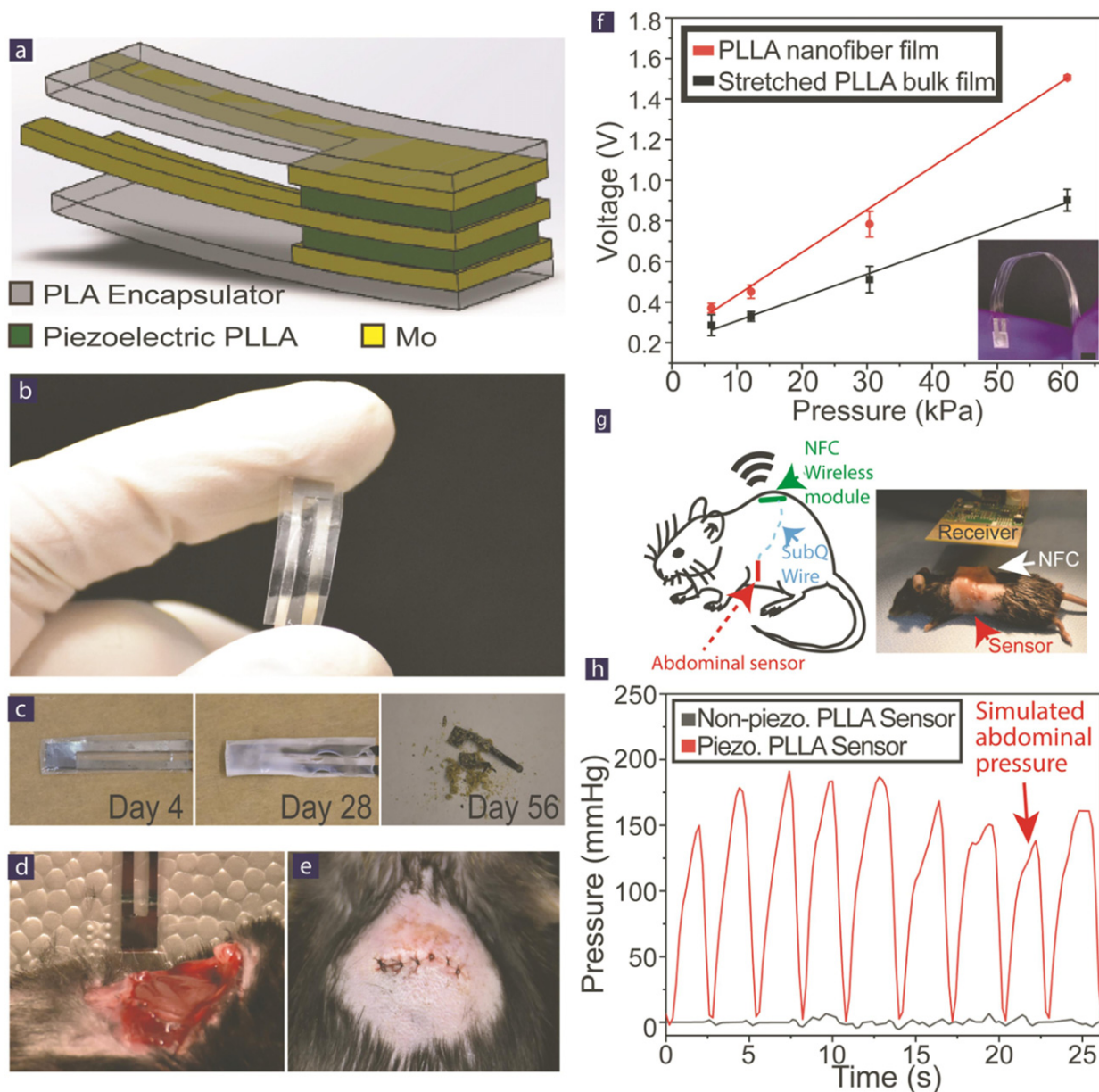


Fig. 5 Biodegradable piezoelectric PLLA pressure sensor. (a) Simplified schematic representing the biodegradable piezoelectric PLLA sensor (b) Optical image of a fabricated biodegradable piezoelectric PLLA sensor (c) Optical images showing the sensor at different days in the buffered solution (d) Optical image illustrates the sensor and a mouse abdominal cavity with diaphragmatic membrane (e) Surgical wound closed up by medical suture on abdomen of the mouse, which received an implanted PLLA sensor. (f) Calibration curves for a biodegradable sensor using stretched, bulk piezo PLLA film and an electrospun PLLA nanofiber film. (g) Simplified schematic of the wireless biodegradable pressure sensor in a mouse and the optical image of the experiment. (h) Comparison of the simulated abdominal pressure signals wirelessly recorded from an implanted biodegradable PLLA nanofiber sensor made from piezoelectric nanofiber film and negative control. Reproduced from Curry, E.J., *et al.*, 2018. Biodegradable Piezoelectric Force Sensor. *Proceedings of the National Academy of Sciences of the United States of America*. Curry, E.J., *et al.*, 2020. Biodegradable nanofiber-based piezoelectric transducer. *Proceedings of the National Academy of Sciences of the United States of America* 117(1), 214–220.

Analysis of the results showed that cell differentiation under electromechanical actuation is larger than mechanical actuation alone. Furthermore, the additive effect of electromechanical actuation on stem cell differentiation is reported, which is a crucial design parameter for engineered scaffolds.

Piezoelectric nanocomposites using PVDF fibers and barium titanate nanoparticles (BTNPs) are investigated by Mota *et al* (Mota *et al.*, 2017) for cochlear stimulation. BTNP/PVDF ultrafine fibers were electrospun and used as novel electromechanical transducers to rebuild cochlear function. To investigate the biocompatibility of the material, OC-k3 epithelial cells were seeded into wells containing nanocomposite fibers (Fig. 4(i)). The epithelial cells exposed intact nuclei in the areas surrounding the fibers, thus indicating their cytocompatibility (Fig. 4(j)). The proliferation of neural cells under dynamic culture using BTNP/PVDF fibers

were observed (Fig. 4(k, l)). Collectively, the obtained findings are vastly suggestive that nanostructured piezoelectric materials will be able to advance the material performance by supporting the tissue/material interaction at targeted cellular levels.

The effect of electrospinning parameters on the piezoelectricity of PVDF nanofiber actuators is investigated by Wang *et al.* (2018). PVDF nanofibers were fabricated using an electrospinning setup and then were pressed to get a smooth surface. The constrained fiber film was sputtered with Au electrodes on both surfaces and then poled in a silicon oil bath under an electric field to achieve high piezoelectricity (Fig. 4(m)). The fabricated actuator under improved electrospinning conditions was then used for implanted energy harvesting in rats (Fig. 4(n)). Since electrospun PVDF-TrFE nanofibers have excellent biocompatibility and a large piezoelectric effect, fibroblast cells developed perfectly along the fiber direction, and the proliferation rate was promoted by 1.6 folds (Fig. 4o, (p)).

Using wireless stimulations to prompt piezoelectricity in polymers to promote differentiation of neuronal cells can create a new road for contactless, precise neuroregenerative therapies. An *in vitro* validation on the effect of ultrasonically stimulated piezoelectric β -PVDF for the neurite production in PC12 cells was provided by Hoop *et al.* (2017). Commercially acquired PVDF membrane was coated with gold electrodes, and then actuated by ultrasonic waves to cause mechanical deformations (Fig. 4(q)). The results showed that the ultrasound is capable to induce polarization in the piezoelectric polymers, therefore, initiating differentiation of PC12 cells (Fig. 4(r)). This study determines that using a combination of ultrasonic actuation and piezoelectric polymers is promising for the differentiation of neuron cells and merit further investigation.

PLLA biodevices

Lactide (cyclic dimer of lactic acid) has three optical isomers including L-lactide, D-lactide, and DL-lactide (Mehta *et al.*, 2005). The polymers obtained from L-lactide, D-lactide, and DL-lactide are abbreviated to PLLA, PDLA, and PDLLA, respectively. In particular, PLLA has a high shear piezoelectric constant comparable to the ferroelectric polymer PVDF, (Tajitsu, 2008) which exhibits highly tensile piezoelectricity. PLLA is a plant-derived polymeric material, transparent and extremely flexible, and is considered suitable for applications in mobile devices as an environmentally friendly, flexible, transparent piezoelectric thin film (Yoshida *et al.*, 2010). However, since its piezoelectric constant is significantly lower than that of inorganic piezoelectric materials such as PZT, the practical application of PLLA is limited. It is reported that elongated PLLA films have no spontaneous polarization, distinct from poled polymers such as PVDF, but still have a sizable shear piezoelectric constant (Ochiai and Fukada, 1998). Piezoelectricity of PLLA increases considerably when a certain level of purity is achieved (Tajitsu, 2016). Although PLLA has a complicated higher ordered structure with intermixed crystalline and amorphous regions, it is feasible to control the degree of crystallinity of PLLA using a thermal annealing process. As a result, the piezoelectric constant of the film can be enhanced by increasing crystallinity and molecular orientation. PLLA as a biodegradable and biocompatible film has many promising applications in the future of BioMEMS devices and sensors.

A. Sensors

The first completely biodegradable piezoelectric force sensor was developed by Curry *et al.* in 2018 (Curry *et al.*, 2018). to examine physiological forces. The piezoelectric PLLA was realized by a stretching/annealing process at 90°C for 8 h. A 3 mm $\times$ 15 mm patch of obtained PLLA was then cleaved at a 45° angle relative to the stretched direction of a draw ratio 4.6 film to form the piezoelectric element of the sensor. The film is folded and compressed between molybdenum electrodes after magnesium/iron deposition on the film. Achieve multilayer design is depicted in Fig. 5(a). The sensor is then placed between sheets of 100 μ m thick PLA and coated with biodegradable PLA glue and a thermal bag sealer. Produced biodegradable PLLA sensor is portrayed in Fig. 5(b). As described in Fig. 5(c), the sensor is entirely corrupted following a period of 56 days at an elevated temperature of 74°C. Due to the biocompatible and biodegradable nature of the exploited materials and the sensor's potential for miniaturization, it can be implanted anyplace in the body with minimal adverse immune response. For instance, they demonstrated that the PLLA piezoelectric sensor can be implanted inside the abdominal cavity of a mouse to inspect the pressure of diaphragmatic contraction (Fig. 5(d,e)).

In addition, recently, Curry *et al.* (2020) have reported a new strategy for processing the material to attain biodegradable, biocompatible PLLA electrospun nanofibers mat with a highly controllable, efficient, and stable piezoelectric performance. The new biodegradable force sensor made from electrospun PLLA film possesses higher flexibility and exhibits higher sensitivity for force detection than a sensor made from compression-molded PLLA (Fig. 5(f)). The sensor's application has been demonstrated in wirelessly monitoring the abdominal pressure in mice (Fig. 5(g)). The device was fully implanted in the abdominal cavity in the mouse and connected to the printed circuit board (PCB), which contains a charge amplifier circuit, a near-field communication (NFC) system, and an antenna for recording and transferring the signal. As shown in Fig. 5(h, a) notable signal was measured by the implanted force sensor while the mouse's abdomen is depressed and relaxed periodically. A less piezoelectric sample was used as a negative control to validate the signal was not generated due to the triboelectricity effect. Accumulatively, the biodegradable force sensor has a wide range of measurable pressures. Moreover, the facile fabrication process compared to photolithography-based sensors, makes the sensor more encouraging for clinical implementation.

Biodegradability is an essential element for the detection of molecules in next generation biosensors. In some severe or short-term medical applications (e.g., wound or bone healing), where sensor is required to be implanted for a limited time, the insertion of biodegradable PLLA sensors could be desirable to prevent the need for a secondary removal surgery. Investigation on PLLA for sensor applications has been reported by several researchers and is under extensive research (Allen, 2014; Boutry *et al.*, 2016; Luo *et al.*, 2014; Luo, 2014; Ando *et al.*, 2013; Koike *et al.*, 2012; Grayson *et al.*, 2003).

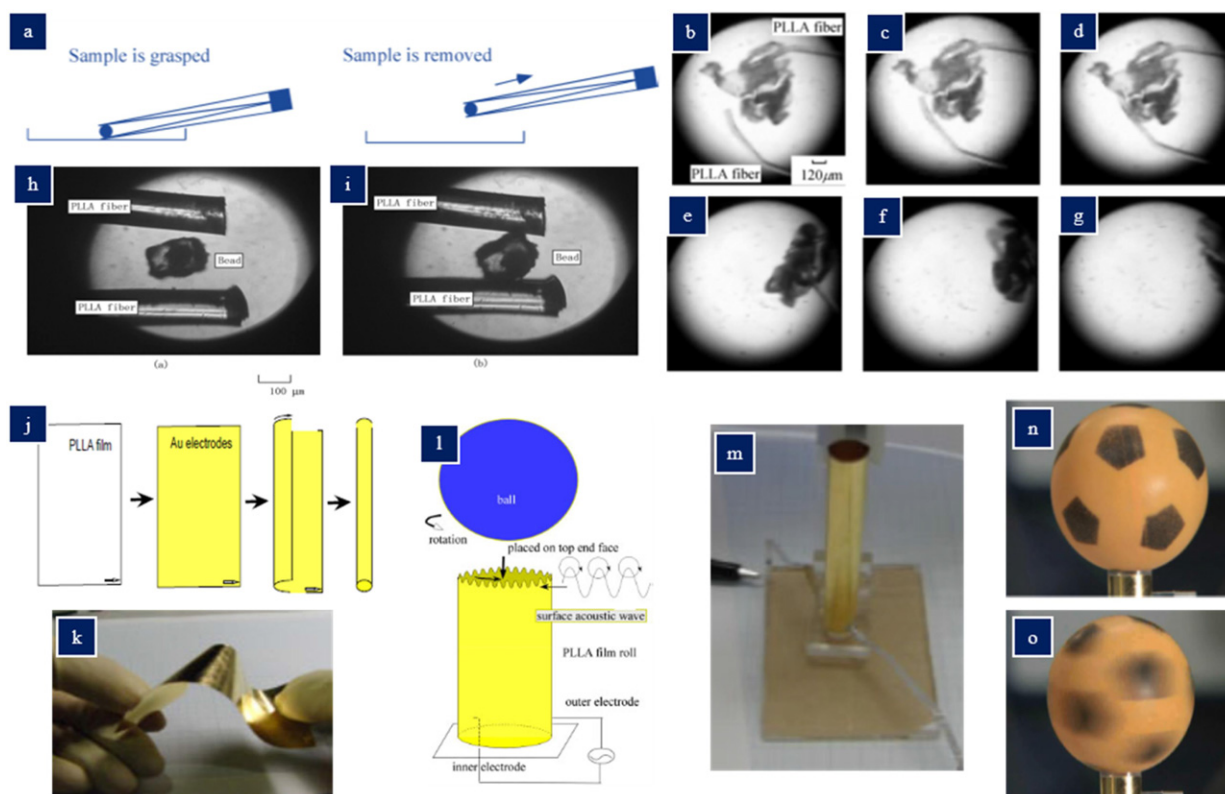


Fig. 6 PLLA-based actuators (a-i): (a) Schematic of demonstration of tweezers (b-d) Photographs showing the grasping of a thrombosis sample using PLLA fibers controlled by applied voltage and (e-g) removal of a thrombosis sample. (h) Releasing a bead and (i) grasping a bead using PLLA fibers with control by applied voltage. (j-o): PLLA-based soft actuator (j, k) Illustration of PLLA film roll actuator (l) Schematic and (m) experimental setup of a ball rotating on the top end face of a PLLA film roll transducer (n, o) A ball rotating on the top end face of a PLLA film roll transducer (n) power off and (o) power on. Reproduced from Tajitsu, Y., *et al.*, 2005. Novel tweezers for biological cells using piezoelectric polylactic acid fibers. *Ferroelectrics* 320(1), 133–139. Tajitsu, Y., *et al.*, 2004. Microactuators with piezoelectric polylactic acid fibers—toward the realization of tweezers for biological cells. *Ferroelectrics* 304(1), 195–200. Tajitsu, Y., 2016. Development of environmentally friendly piezoelectric polymer film actuator having multilayer structure. *Japanese Journal of Applied Physics* 55(4S), 04EA07.

B. Actuators Stimulators and Ultrasound Transducer

Actuators that are biocompatible, biodegradable, and flexible are now essential in various biomedical fields. PLLA as a light and biodegradable film with a large shear piezoelectricity is the currently the most appropriate material to take on the task and achieve these requirements.

Tajitsu *et al.* in a series of papers (Tajitsu, 2006; Tajitsu *et al.*, 2005, 2004; Sawano *et al.*, 2010) utilized the piezoelectric properties of PLLA to develop a biodegradable tweezer which can be implanted into the body through a catheter for the treatment of thrombosis. Fig. 6(a) illustrates the operating principle of this simple tweezer. The PLLA fibers were attained using electrospinning process and further actuated via externally applied AC voltage. To demonstrate its ability to grasp a blockage due to thrombosis, the PLLA tweezer was inserted into a blood vessel (Fig. 6(b-d)), and was subsequently removed (Fig. 6(e-g)). The tweezer also demonstrated its potential to release and grasp a silica bead (Fig. 6(h, i)). With great biocompatibility, biodegradability and high sensitivity, PLLA tweezers could find applications in cellular biology, tissue engineering, nanomedicine, and cell delivery.

A novel type of soft actuator using PLLA was developed by Tajitsu *et al.* (2016); Inuzuka *et al.*, (2012); Tajitsu (2013, 2012) to use the generated surface waves as an actuation force. The transducer was synthesized by sandwiching the PLLA film between two gold electrodes, and then rolling it into a long thin roll (Fig. 6(j, k)). Due to the shear piezoelectric effect of PLLA and negligible end face of the rolled PLLA, the end face of the PLLA film produces acoustic surface wave. Figs. 6(l and m) show a schematic and the device setup of the experiment, respectively. They used the soft actuator to rotate a plastic ball (Fig. 6(n, o)). Further studies are needed to investigate the future applications of soft actuators.

PLLA has also been utilized to fabricate an ultrasonic transducer thanks to its piezoelectricity. Curry *et al.* (2020). have reported the ability of the piezoelectric electrospun nanofibers PLLA to generate and respond to the ultrasonic waves. For proof of concept, the potential application of this biodegradable PLLA ultrasound transducer has been illustrated for disrupting the blood-brain barrier (BBB); the device then safely self-degrades and causing no harm to the body (Fig. 7(a)).

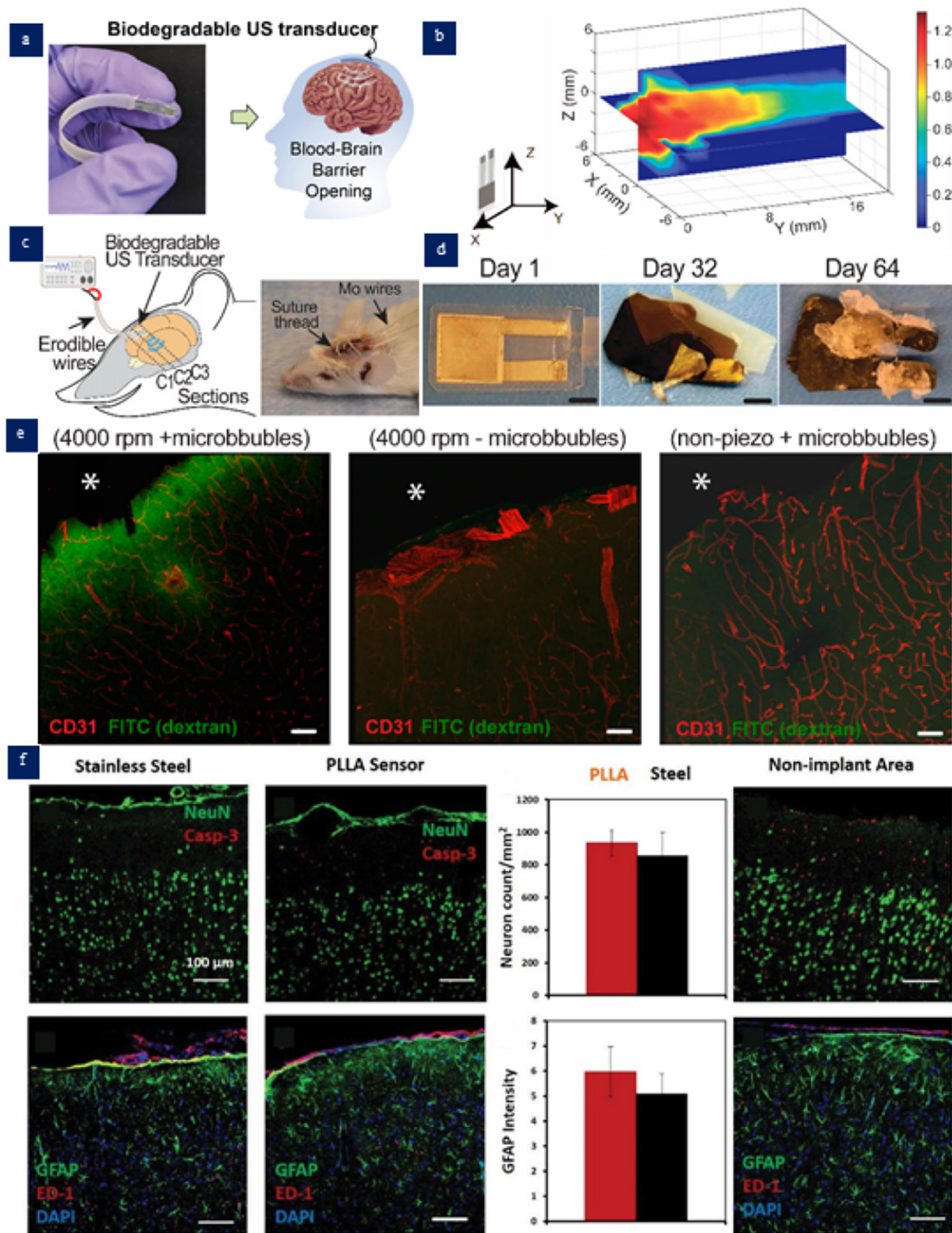


Fig. 7 Biodegradable piezoelectric PLLA ultrasound transducer (a) Simplified application of the piezoelectric transducer in disrupting the blood-brain barrier. (b) The spatial pressure field of the PLLA piezoelectric transducer. (c) The diagram of the *in vivo* experiment in mice. On the right is an optical image of the mouse head, receiving the implanted US transducer with the wound closed via medical suture (d) The optical images of a typical biodegradable US nanofiber transducer at different days in the buffered solution at an accelerated-degradation temperature of 70°C. Scale bars are 5 mm. (e) Representative images show the signal of dextran (FITC) at the coronal sections from the brains of mice that received treatment from the 4000-rpm transducer with the microbubbles (left), the 4000-rpm transducer without the microbubbles (center), and the non-piezoelectric (300 rpm) transducer with the microbubbles (right). The asterisk (*) shows the position of the implanted device. Scale bars are 50 μ m. (f) Immuno-histochemistry staining of brain tissue shows biocompatibility of the PLLA transducer for 4-week brain implantation. Reproduced from Curry, E.J., *et al.*, 2020. Biodegradable nanofiber-based piezoelectric transducer. *Proceedings of the National Academy of Sciences of the United States of America* 117(1), 214–220.

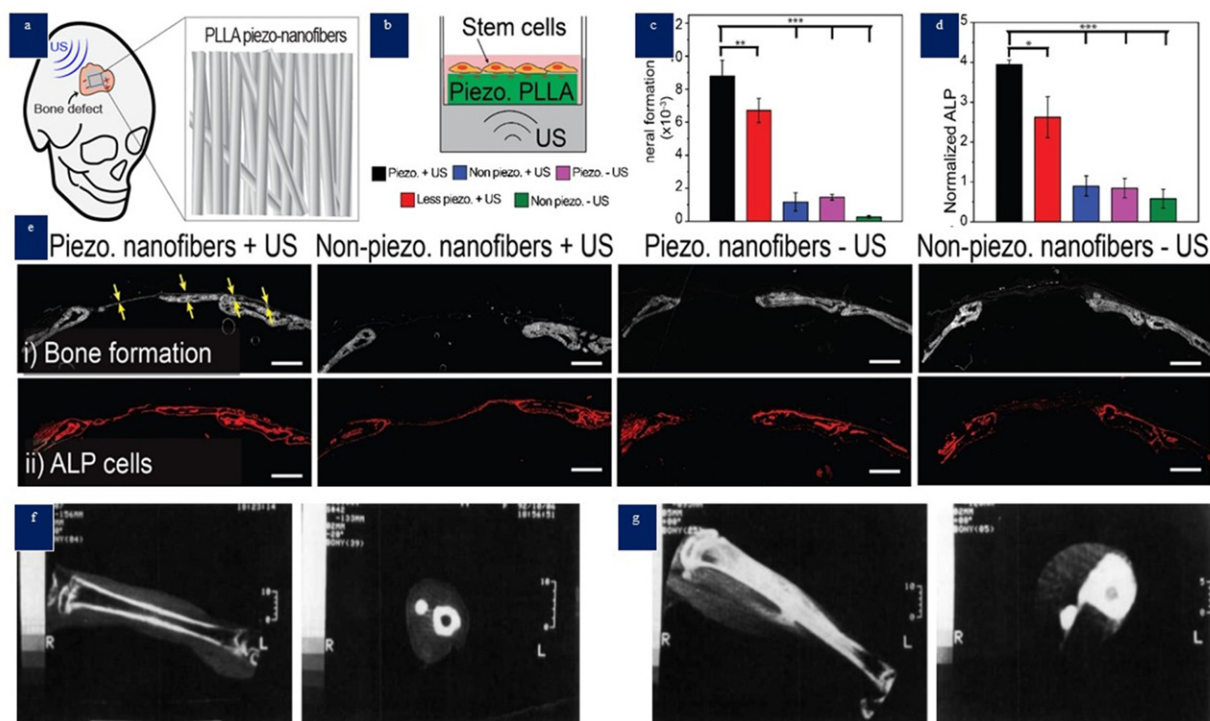


Fig. 8 PLLA-based tissue stimulators (a) Simplified application of the piezoelectric nanofiber mat in combination with acoustic-pressure (from non-invasive ultrasound) and schematic of the placement of aligned nanofibers in the scaffold. (b) A simple schematic demonstrates the setup for seeding adipose stem cells (ADCSs) onto the scaffolds and treating them with US. (c) A quantitative comparison of ALP production by the cells in different treatment groups. (d) shows mineral formation by the cells, quantitatively, as measured by the alizarin red assay. (e) Representative histology sections of the mouse calvarial bone showing details of bone formation and cell migration into the defects for different groups. e.i. Aperture contrast images comparing the mineral formation in the defect between the two mice. e.ii. Microscopic fluorescent images comparing the presence of ALP producing cells in the defect between the two mice using vector blue ALP staining (f, g): X-ray CT photographs of the tibiae of cats at 8 weeks after implantation of rods of different materials (f) Undrawn PLLA (g) Drawn PLLA (draw ratio = 4). Reproduced from Ikada, Y., *et al.*, 1996. Enhancement of bone formation by drawn poly (L-lactide). *Journal of Biomedical Materials Research Part A* 30(4), 553–558.

The PLLA nanofibers film is prepared by electrospinning and then goes through careful annealing to achieve high and stable piezoelectricity. An air-backed, unfocused ultrasound transducer was fabricated by sandwiching the piezoelectric PLLA nanofiber mat between two molybdenum electrodes, then encapsulating in compression molded PLLA layers. **Fig. 7(b)** shows the spatial pressure field of the biodegradable transducer at 1 MHz. In order to certify the potential application of the biodegradable transducer in facilitating the delivery of drugs across the BBB, dextran is used as a drug model for administering to the animal. The schematic of the experiment is described in **Fig. 7(c)**. The PLLA transducer functions well in its predefined lifetime and eventually self-degraded (**Fig. 7(d)**). The functional lifetime of the device can be engineered by tailoring the encapsulating materials. As seen in **Fig. 7(e, a)** a remarkable level of the green signal of dextran was found around the microvessels in the brain of mice that received the ultrasound treatment generated by the PLLA transducer. It is noticeable that the intensity of the dextran is reduced at deeper areas of the brain. On the other hand, no signal was found on the coronal sections of the 2 control samples. Furthermore, the biocompatibility of the PLLA devices is demonstrated by implanting the device into the intracranial cavity of rats for histology analysis. The histological images showed the device elicits minimal fibrosis and immune response after implantation for 4 weeks (**Fig. 7(f)**). These results collectively illustrate that the biodegradable PLLA transducer can be implanted safely into the brain to open the BBB locally and effectively. The transducer can degrade, causing no harm to the body and avoiding invasive brain surgery for removal.

C. Tissue Stimulators

There have been abundant attempts to use the biocompatible and biodegradable piezoelectric PLLA polymer as a tissue stimulator to promote the proliferation and differentiation of cells. Das *et al.* (2020) developed a bone scaffold from using a PLLA nanofiber scaffold containing highly aligned PLLA fiber (**Fig. 8(a)**). The scaffold was synthesized by electrospinning using a collector drum that rotated at a very high speed (up to 3000 rpm). It was shown that the drum speed had a direct correlation to the fiber alignment and piezoelectric output of the PLLA nanofiber mat. The authors used this nanofiber mat in combination with ultrasonic vibrations to generate bone tissue both at *in vitro* and *in vivo* levels. They used adipose-derived stem cells *in vitro* to show

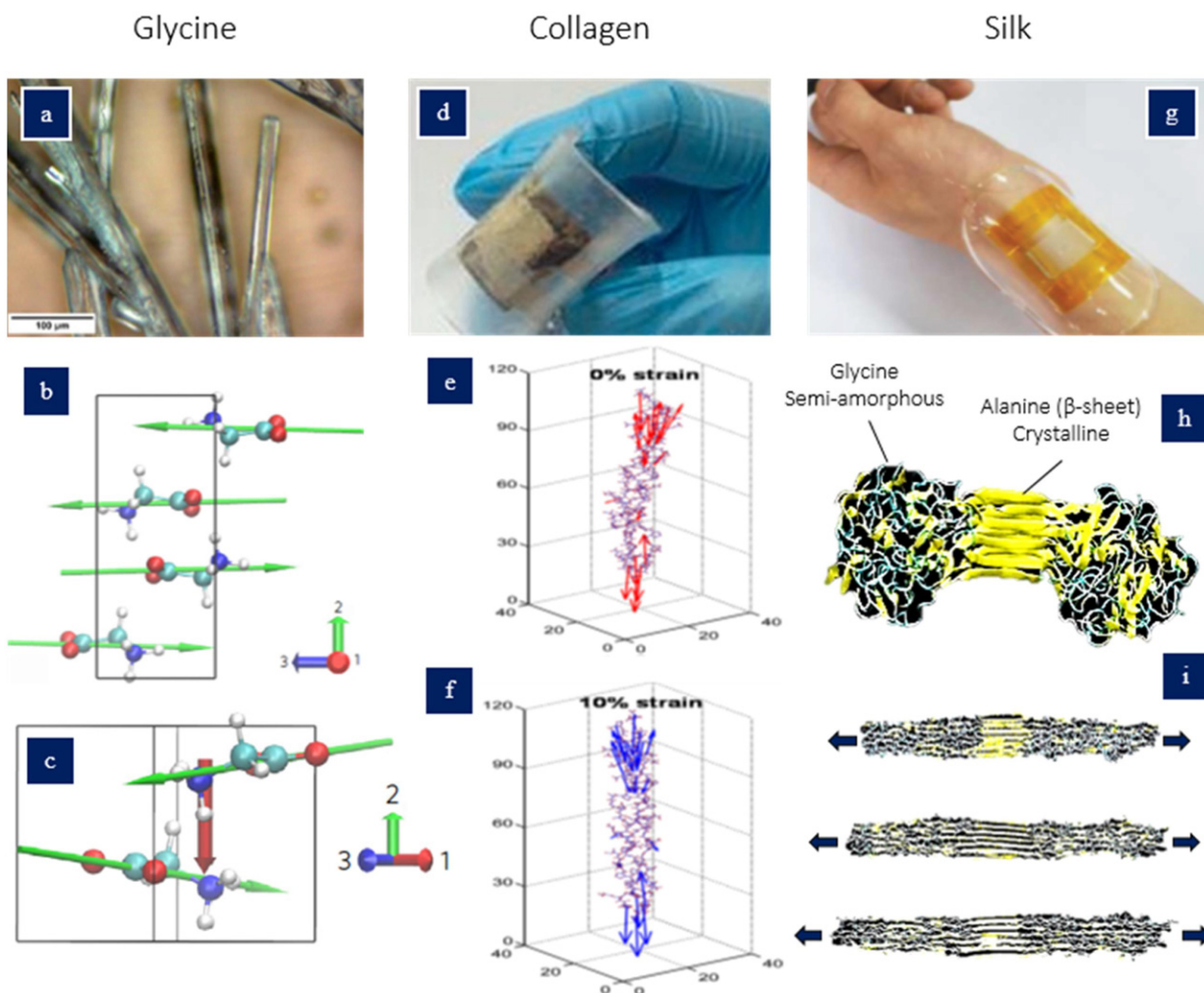


Fig. 9 Potential organic piezoelectric biomaterials (a-c): Piezoelectric response in glycine amino acid crystals. (a) Image showing β -glycine needles (b) The molecular dipoles (green arrows) in α -glycine sum to zero and produce no net polarization. (c) Molecular dipoles in the unit cell (red arrow) of β -glycine sum to a spontaneous polarization. (d-f): Molecular origin of the piezoelectric effect in collagen. (d) Photograph of the collagen-based flexible sensor. (e) Changes of dipole moment vectors in a collagen molecule before and (f) after uniaxial tension. (g-i): Origins of silk piezoelectricity. (g) Photograph of the silk device for detection of wrist pulses. (h) The molecular structure of spider silk in its natural state, without mechanical load applied, and (i) the molecular structure under varying (increasing) stress, showing how the protein chains unwind under stretch. Reproduced from Guerin, S., *et al.*, 2017. Control of piezoelectricity in amino acids by supramolecular packing. *Nature Materials*. Ghosh, S.K. and D. Mandal, 2017. Sustainable energy generation from piezoelectric biomaterial for noninvasive physiological signal monitoring. *ACS Sustainable Chemistry & Engineering* 5(10), 8836–8843. Zhou, Z., D. Qian, Miny-Jolandan, M., 2016. Molecular mechanism of polarization and piezoelectric effect in super-twisted collagen. *ACS Biomaterials Science & Engineering* 2(6), 929–936. Wang, X., *et al.*, 2014b. Silk-molded flexible, ultrasensitive, and highly stable electronic skin for monitoring human physiological signals. *Advanced Materials* 26(9), 1336–1342. Bratzel, G., Z. Qin, Buehler, M.J., 2013. Viscoelastic relaxation time and structural evolution during length contraction of spider silk protein nanostructures. *MRS Communications* 3(3), 185–190. Tarakanova, A. and M.J. Buehler, 2012. A materiomics approach to spider silk: Protein molecules to webs. *JOM* 64(2), 214–225.

that cells cultured on the piezoelectric nanofiber mat and stimulated with ultrasound (Fig. 8(b)) produced more alkaline phosphatase enzyme (Fig. 8(c)), bone minerals (Fig. 8(d)), and expressed more osteogenic genes like osteocalcin and osterix. In addition, they also demonstrated higher osteogenic differentiation using bone marrow stem cells by looking at the expression of osteogenic proteins like bone sialoprotein and dentin matrix protein. *In vivo*, they used a murine calvarial defect model to show bone regeneration. The defects on the calvarial bone of mice were covered with the nanofiber mat and stimulated with ultrasound for several weeks. Six weeks post-surgery, the mice with the piezoelectric implant receiving ultrasound stimulation showed significant bone formation in the defect area (Fig. 8(e)). Besides bone, the PLLA nanofiber mats can be fabricated into a piezoelectric scaffold which can be activated by exercise-induced joint loads to produce electrical cues for promoting cartilage regeneration. (Liu *et al.*, 2022)

It has also been shown that implanted drawn (piezoelectric) PLLA rods in the intramedullary cavity of feline tibiae of cats shape significantly higher callus in contrast to undrawn (nonpiezoelectric) PLLA rods (Fig. 8(f, g)) (Ikada *et al.*, 1996). Based on the

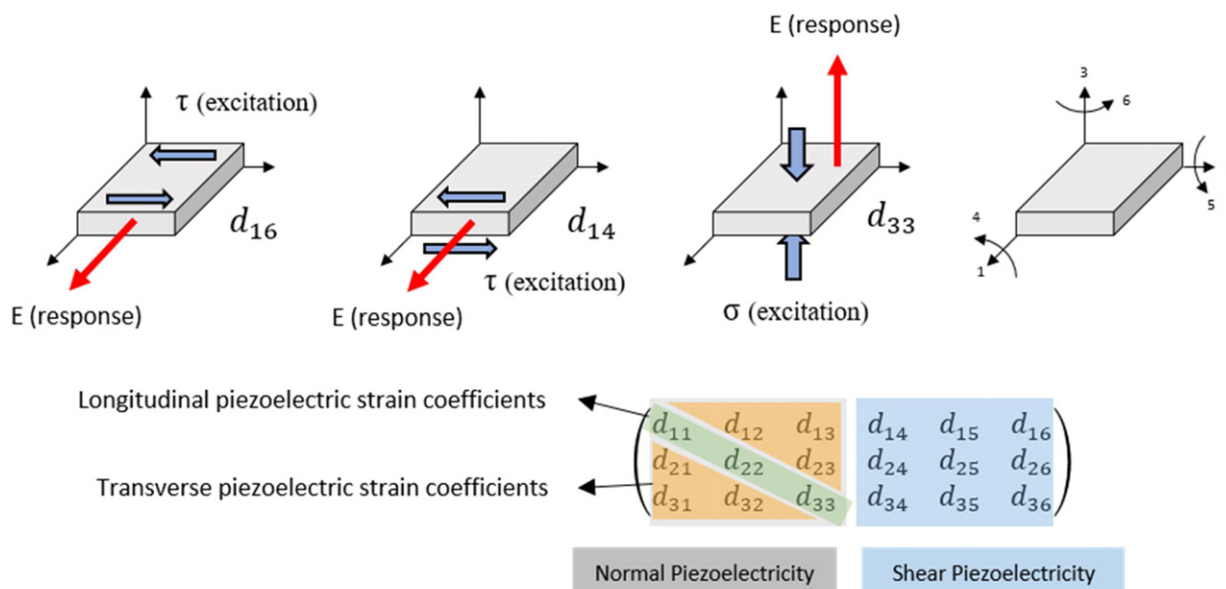


Fig. 10 Relationship between applied normal (σ) and shear (τ) stress and corresponding induced electric field (E).

observations, fracture healing was clearly improved due to the increased callus formation as the draw ratio of the PLLA rod increased. This finding strongly indicates that the drawn PLLA can deliver improved fracture fixation devices. Furthermore, because it is resorbable in the body, a second surgery is unnecessary.

Potential applications from other piezoelectric organics

The use of piezoelectric polymers in different BioMEMS applications is beginning to gain attention due to particular properties that polymers possess in comparison to inorganic materials. Organic piezoelectric materials like glycine, collagen and silk have attracted attention in recent years. Glycine (**Fig. 9(a)**) is a polymorphic amino acid and can construct three dissimilar crystalline structures depending on the crystallization conditions; α , β and γ structures (Litaka, 1959). α -glycine is centrosymmetric, and thus non-piezoelectric (**Fig. 9(b)**) (Guerin *et al.*, 2017). β - and γ -glycine have acentric structures and exhibit shear piezoelectricity (**Fig. 9(c)**) (Isakov *et al.*, 2011). The shear piezoelectric coefficients of β -glycine can surpass the magnitudes of any piezoelectric coefficient of γ -glycine. The piezoelectric strain constant and piezoelectric voltage constant of β -glycine were determined to be around $d_{16} = 190$ pm/V and $g_{16} = 8$ Vm/N, respectively (Guerin *et al.*, 2017). This high piezoelectricity along with biocompatibility and well-regulated biodegradability make glycine extremely suitable for biomedical and biotechnological applications.

Piezoelectric collagen (**Fig. 9(d)**) is especially exciting since there are currently several FDA-approved biomedical devices that use different forms of collagen (Fukada and Yasuda, 1964). It is possible to fabricate self-powered collagen-based implantable devices. The origin of piezoelectric effect in collagen originates from polar and charged groups in the molecule (Zhou *et al.*, 2016). Under mechanical stress, the induced dipole moments of these residues reorient about the long axis of the collagen molecule and the degree of the dipole moments change (**Fig. 9(e, f)**). Together these properties result in the inclusive piezoelectric effect in collagen (Zhou *et al.*, 2016). The shear piezoelectric constant of collagen is reported to be around $d_{14} = 0.1$ pm/V, (Minary-Jolandan and Yu, 2009) but recent studies tend to increase this value by adding chitosan (Silva *et al.*, 2001) or by adjusting the pH from acidic to neutral (Denning *et al.*, 2014). Collagen is a biocompatible and biodegradable protein, and the most abundant protein in mammals. Merging these properties with its advantageous electromechanical properties could be an interesting route toward future applications for implantable biomedical devices for long-term monitoring of physiological effects.

Silk (**Fig. 9(g)**) in its raw state comprises of an inner fibroin core enclosed with an outer protein known as sericin. Silk is identified to have a combination of amorphous and crystalline nature (Joseph *et al.*, 2017). The crystalline regions are either silk-I (metastable and water-soluble) or silk-II (stable and water-insoluble) (Drummy *et al.*, 2005). Silk-I is composed of primarily α -helix structures and silk-II is generally composed of β -sheet structures due to the dominance of hydrophobic domains (Joseph *et al.*, 2017; Vepari and Kaplan, 2007). Fukada quantified the intrinsic shear piezoelectricity of silk fiber bundles (Fukada, 1956). Overall, the silk piezoelectricity is a result of combination of a high degree of silk II, β -sheet crystallinity and crystalline orientation (**Fig. 9(h, i)**) (Yucel *et al.*, 2011). Silk films with draw ratio = 2.7 demonstrate shear piezoelectric coefficients of $d_{14} = -1.5$ pC/N (Yucel *et al.*, 2011). Silk fibroins have established its usage in tissue engineering, (Wang *et al.*, 2006) regenerative medicine, (Yang *et al.*, 2007) and bone fracture healing (Meinel *et al.*, 2006).

Cellulose is an abundant, natural and biodegradable polymer and is a linear-chain polysaccharide that consists of several hundred to thousands of glucose subunits linked one to another through β -1,4-glucosidic bonds (Basta *et al.*, 2016). The crystallinity of cellulose is formed due to the strong hydrogen bonds of the hydroxyl groups in its structure (Park *et al.*, 2010). The piezoelectric

Table 1 Comparison of piezoelectric coefficients for different biocompatible piezoelectric materials.

<i>Piezoelectric Biomaterial</i>	<i>Pros</i>	<i>Cons</i>	<i>Material Type</i>	<i>Piezoelectric Constants</i>	<i>References</i>
PZT-5 H	1. High piezoelectricity 2. High operating temperature	- Contains lead	Ceramic	$d_{33} = 593$ [pC/N], $d_{31} = -274$ [pC/N]	(Bystrov <i>et al.</i> , 2012)
AlN	1. High acoustic velocity 2. High resonance frequency	- Expensive	Ceramic	$d_{33} = 3\text{--}6$ [pC/N], $d_{31} = -2$ [pC/N]	(Guy <i>et al.</i> , 1999)
Quartz	- Long term stability	- Cannot work well in low and high temperature environment	Crystal	$d_{11} = 2.3$ [pC/N], $d_{14} = -0.67$ [pC/N]	(Newnham, 2005)
ZnO	1. Excellent transparency 2. High electron mobility	- Requires very high processing temperature	Crystal	$d_{33} = 6\text{--}13$ [pC/N], $d_{31} = -5$ [pC/N]	(Someya, 2012)
BaTiO ₃	- Ferroelectric	- Brittle and inelastic	Ceramic	$d_{33} = 190$ [pC/N], $d_{31} = -78$ [pC/N]	(Newnham, 2005)
LiNbO ₃	1. Ferroelectric 2. High spontaneous polarization	- Brittle	Ceramic	$d_{33} = 16$ [pC/N], $d_{31} = -1$ [pC/N]	(Newnham, 2005)
PMN-PT	- High piezoelectricity	- Fragile	Crystal	$d_{33} = 2000\text{--}3000$ [pC/N]	(Someya, 2012)
GaN	- Large energy bandgap	1. Low thermos conductivity 2. hard to fabricate large size and high quality of GaN	Crystal	$d_{33} = 2\text{--}4$ [pC/N], $d_{31} = -1.5$ [pC/N]	(Guy <i>et al.</i> , 1999)
PVDF	- High piezoelectricity among polymers	- Explore in high pressure or temperature	Polymer	$d_{33} = -33$ [pC/N], $d_{31} = 23$ [pC/N]	(Someya, 2012)
PLLA	- Biodegradable	1. Weak resilience 2. Acidic degradation products	Polymer	$d_{14} = 6\text{--}12$ [pC/N]	(Tajitsu, 2008)
β -Glycine	1. High piezoelectricity 2. Biodegradable	- Hard to fabricate	Crystal	$d_{16} = 195$ [pm/V]	(Guerin <i>et al.</i> , 2017)
Collagen	1. Natural material 2. Biodegradable	- Low piezoelectric constant	Non-oriented	$d_{14} = 0.1$ [pm/V]	(Minary-Jolandan and Yu, 2009)
Silk	- Biodegradable	- Low piezoelectric constant- Expensive	Polymer	$d_{14} = -1.5$ [pC/N]	(Yucel <i>et al.</i> , 2011)

activity of cellulose is a result of lacking symmetrical atoms in the centers in monoclinic and triclinic crystallinity combined with high polarity hydroxyl groups which induce asymmetric dipole structures with a shear piezoelectric coefficient $d_{14} = 0.2$ pC/N (Kim *et al.*, 2006). With an excellent environment that promotes cell adhesion and growth, (Pétille *et al.*, 2012) tunable physical, and mechanical properties, (Courtenay *et al.*, 2018) cellulose has highly impacted tissue regeneration and biomedical application that including cartilage, (Hickey *et al.*, 2018) tendon/ligament, (Mathew *et al.*, 2013) skin, (Hakkarainen *et al.*, 2016) bone, (Park *et al.*, 2015) nerve, (Naseri-Nosar *et al.*, 2017) larynx regeneration (de Souza *et al.*, 2011). Therefore, piezoelectric cellulose material could be a potential candidate for medical self-power sensors, wearable sensors, and cardiac tissue regeneration. To understand better the shear piezoelectricity, the relationship between applied normal (σ) and shear (τ) stress and corresponding induced electric field (E) is shown in Fig. 10. Furthermore, an overall view on all piezoelectric materials, presented herein, is described in Table 1 which provides a comparison of piezoelectric coefficients for different biocompatible piezoelectric materials.

Conclusion and Future Outlook

In summary, piezoelectric biomaterials as a distinctive class of functional materials can convert mechanical deformation into electricity and vice versa. Those materials are or can be biocompatible for use in different biodevices. This book chapter reviewed the working principle of different types of piezoelectric biomaterials used in biosensors, bioactuators and tissue stimulators. State-of-the-art biocompatible piezoelectric materials have been reported in the literature with the focus on material properties. A comparison between different piezoelectric biomaterials including organic and inorganic piezoelectrics have also been presented. Each of these materials must be chosen based on the application. Extra improvements are needed to transform them into useful biomedical devices. While inorganic piezoelectric materials have been widely explored, organic piezoelectric biomaterials offer a unique choice, particularly in biosensing applications due to their excellent properties of being mechanically flexible, and biocompatible.

Several key challenges need to be addressed for better use of both inorganic and organic piezoelectric in medicine. These include (1) how to make extremely efficient piezoelectric inorganics such as PZT more biocompatible. (2) how to improve modest piezoelectric constants of organic materials, and (3) how to achieve a robust control over dissolution rate of some biodegradable piezoelectric polymers (e.g. PLLA, silk etc.). Solutions to the first problem can include the use of biocompatible encapsulators or fabricating lead-free piezoelectric inorganics (Deutz *et al.*, 2017; Kim *et al.*, 2017; Yokozawa *et al.*, 2018). For the second problem, piezoelectricity in organic polymers can be enhanced by creating composites, mixing together organic and inorganic materials, or creating multi-layer piezoelectric devices (Xu *et al.*, 2017; Chatzinikolaïdou *et al.*, 2015; Kim *et al.*, 2018). To resolve the third challenge, biodegradable piezoelectric polymers can be treated under different conditions (e.g. different temperatures or stretching ratios or poling electrical-fields) which will assist ones to engineer their degradation rate (Guo *et al.*, 2017; Kikkawa *et al.*, 2017; Surwase *et al.*, 2017).

Despite such challenges, the field of piezoelectric biomaterials is gaining interest at a fast pace with growing applications in the development of BioMEMS and other biomedical devices. We believe recent advances in piezoelectric biomaterials will bring innovative, major diagnostic tools and effective treatments in medicine.

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Organic Bioelectronic Sensors

Annalisa Bonfiglio, Department of Electrical and Electronic Engineering, University of Cagliari, Cagliari, Italy and Scuola Universitaria Superiore, IUSS - Pavia, Italy

Piero Cosseddu and Stefano Lai, Department of Electrical and Electronic Engineering, University of Cagliari, Cagliari, Italy

Andrea Spanu, Scuola Universitaria Superiore, IUSS - Pavia, Italy

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Abstract

Organic biosensors are a class of devices specifically designed for the detection and quantification of bioanalytes and/or chemical-physical parameters whose variations occur within a biologically relevant environment. They provide the electronic transduction of chemico-physical properties by means of devices that, thanks to the peculiar properties (i.e., mechanical flexibility, ionic conductance) of organic materials, are biocompatible in a very broad sense, i.e., not only safe for biological tissues but also because they share with them a complete material affinity. For this reason, they are revolutionizing the world of biosensors, paving the way to a variety of novel tools for applications including electrophysiology, bioanalytical chemistry, brain-machine interfaces.

Key Points

- An introduction to the organic transistors, basic block of organic biosensors.
- A panoramic view of the main applications:
- Bioanalytical sensors.
- Cell Biosensors.
- Physical sensors for biological environment.

Introduction

According to the traditional definition, biosensors are analytical devices used for the detection of a chemical/physical agent, that combine a biological component with a physicochemical detector. According to this definition, this class of devices should include any analytical tool that exploits the capability of a certain biological probe, included in the device structure, to recognize a biological target in an unknown mixed environment, typically a liquid solution, no matter of the particular transduction principle employed for the translation of the chemical signal into a measurable variable.

The evolution of the bioanalytical field led to the extension of the definition of biosensors to those tools that, though not including a biological agent in the structure, are able to provide a transduction of the analytical biosignal into another kind of measurable signal or, alternatively, can provide analytical information about a biologically relevant environment. To this aim, a variety of transduction principles have been identified, going from gravimetric, to nanomechanical, from optic to electronic. In the case of electronic sensors, the transduction is based on the electronic interaction between the sensing portion of the device and the ambient hosting the analyte (or where the physical parameter is varying in case of physical sensors). More in particular, as the final quantitative variable is an electrical signal, this transduction principle represents the best choice for signal elaboration and data storage. However there are several constraints to consider to design an efficient bioelectronic sensor: the most important is that the recognition event between the receptor and the analyte (or, the configuration variation of the sensing element as a response to a variation of a physical parameter in the environment) must turn into a measurable variation of an electrical parameter of the device, e.g., a current or a voltage. Many examples of bioelectronic sensors have been presented in the past: in the beginning, many were based on the electronic transduction properties of inorganic materials, in particular metals and semiconductors. However, inorganic materials bear a great limitation when employed in monitoring systems for biological environments: as a matter of fact, these materials do not match with bioanalytes both for their electronic properties (electrons vs. ions) and for the mechanical mismatch (rigid vs. soft matter). The need of material affinity has been therefore the main motivation for the emerging of a new field of research, Organic Bioelectronics, that is now starting to generate many successful examples of advanced biosensing devices.

In the following paragraphs, a general introduction to organic field effect transistors is given, aiming at showing to the reader the basic working principle of a variety of devices that have been so far employed as sensors. Afterwards, the focus will be shifted to the main applications that have so far been developed for this kind of devices, namely bioanalytical sensors, sensors for cellular interfacing, and physical sensors.

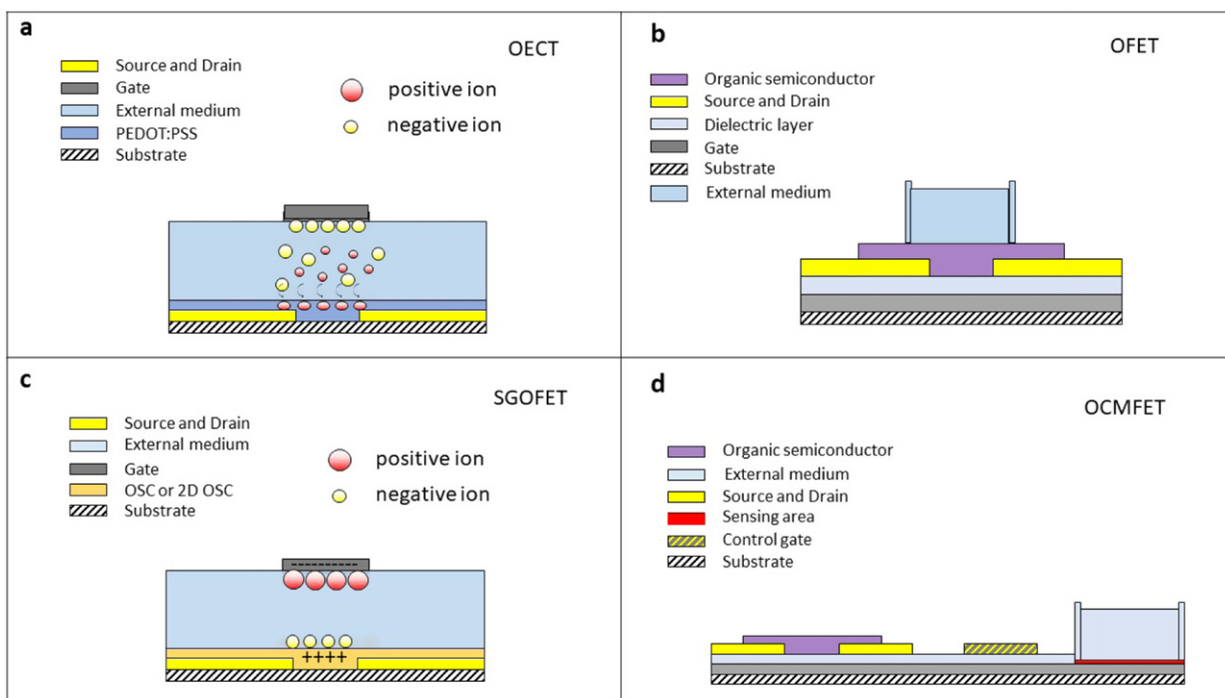


Fig. 1 Schematic view of the four transistor structures mentioned in the paper, and namely: the Organic Electrochemical Transistor (OEET); the Organic Field Effect Transistor (OFET), the Solution-Gated Organic Field Effect Transistor (SGOFET); the Organic Charge Modulated Field Effect Transistor (OCMFET).

Organic Transistors

Organic transistors are the basic block for a variety of sensors. In particular, two mechanisms are currently exploited for this kind of applications: electrochemical gating and field effect, giving rise respectively to the Organic ElectroChemical Transistor (OEET) and to several Field Effect Transistor (FET) structures, namely the Organic Field effect Transistor (OFET) in its standard configuration, the Solution-gated Organic Field effect Transistor (SGOFET) and the Organic Charge Modulated Field Effect Transistor (OCMFET). In the following picture (**Fig. 1**), (a) schematic view of these four organic transistors is given, followed by a more detailed description.

The Organic ElectroChemical Transistor (OEET)

The OEET is a three-terminal device with two electrodes, source and drain, connected through an organic active material, and a third electrode, called gate, that is separated from the channel by an electrolyte (which is an integral part of the transistor). Its working principle is related to the modulation of the doping state of the active material and, consequently, of the channel conductivity caused by the injection of ions from the electrolyte into the organic active material, due to the application of a proper gate voltage (V_G) as shown in the previous figure.

Organic Conductive Polymers (CPs) are usually employed in these devices because of their both ionic and electronic conductivity, chemical tunability, biocompatibility, optical transparency and mechanical flexibility ([Strakosas et al., 2015](#)). The main characteristic of an OEET is therefore the possibility to convert the ionic flow produced by biological agents (from whole cells to single protein channels) into an electronic current. The main characteristics of these transistors are the ultra-low operating voltage (below 1 V), which represents an important feature, especially for their application in liquid environments, and the high transconductance g_m ([Kergoat et al., 2012a](#); [Rivnay et al., 2018](#)):

$$g_m = \frac{\partial I_D}{\partial V_G} = \left(\frac{W}{L} \right) \cdot \mu \cdot d \cdot C^* \cdot (V_G - V_{th})$$

where W and L are the width and the length of the channel, μ is the charge carriers' mobility, V_{th} is the threshold voltage of the device, d is the thickness of the CP layer, and C^* is its volumetric capacitance. Typical CPs employed as active materials of OEETs are: *polypyrrole*, *polyaniline*, *polythiophene*, and *PEDOT:PSS*. In particular, the recent rise of the latter has been driven by its relatively high conductivity, its biocompatibility and good chemical stability, and by its convenient processability ([Wen and Jingkun, 2017](#)).

Organic Field Effect Transistors (FETs)

The structure of a FET is quite similar to that of an OECT. The active channel of an organic field effect transistor is made of a semiconductor layer included between two contacts, source and drain. Differently from the OECT, the gate is here separated from the semiconductor by a thin insulating layer. The voltage applied to the gate, through a purely capacitive effect across the insulating layer, modulates the concentration of charge carriers in the channel, and, as a consequence, the current can flow from source to drain when a potential difference is applied between them. The gate voltage may take any value beyond the so called threshold voltage, that is the minimum voltage required to induce a full conductive channel between source and drain, i.e., is the threshold value separating the off and the on states of the device. The drain current is expressed by two different formulas, according to the working regime of the device. In saturation (i.e., when the absolute value of V_D is higher than the overthreshold voltage), the current is independent of the drain voltage and quadratically dependent on the gate voltage, while in the linear regime (i.e., when the saturation condition is not satisfied), the current is linearly dependent on V_D and V_G .

$$I_D = \frac{1}{2} C_{ox} \frac{Z}{L} \mu (V_G - V_{th})^2$$

$$I_D = C_{ox} \frac{Z}{L} \mu (V_G - V_{th}) V_D$$

In the latter formulas, C_{ox} is the Capacitance per unit area of the dielectric layer, W/L the aspect ratio of the semiconductor channel, and μ is the charge carriers' mobility.

In its standard configuration, exploiting the sensitivity of the semiconductor layer, the OFET structure can be employed for sensing applications, including cell activity sensing with the cells directly grown on top of the semiconductor, chemical sensing and physical sensing. One of the main advantages of employing these devices for sensing applications is that they are multi-parametric devices, meaning that many different electronic parameters (mobility, threshold voltage, contact resistance, etc.), not just one as in two terminal devices sensors, can be extracted from their electrical characterization. OFETs offer the possibility of using a combination of variables to characterize their response to the parameter to be sensed. Moreover, active sensors combine in the same device both switching and sensing functions, and the electrical response of the device to a certain external stimulus can be locally amplified by the transistor itself, allowing the user to easily obtain sensing matrices of limited size and improved reliability. Another important feature is that an OFET is a multilayered structure dominated by the physical properties of several material interfaces, each of which can be employed to test different parameters; as a consequence, it is virtually possible to use a single device to achieve multimodal sensing ability. In addition, thanks to the possibility offered by the peculiar materials employed in organic electronics, OFETs can be relatively easy to fabricate using biocompatible, flexible, and optically transparent materials, and with large area fabrication techniques that help lowering their cost and environmental impact.

Although very interesting devices, standard OFETs present several limitations for sensing applications, due to the usually high operating voltages, the extreme sensitivity of organic semiconductors to humidity and oxygen, and, when they are operated in a liquid environment, the usual need of an external reference electrode immersed directly in the medium where the sensing takes place. Therefore, during the past decade, different approaches have been explored with the intent of fully exploiting the interesting features of organic semiconductor-based active devices. Lately, two types of organic FETs emerged as promising candidates for the development of new generations of cellular bioelectronic interfaces: the solution-gated transistors, with their ultra-high gate capacitance and ultra-low operating voltages, and the Organic Charge Modulated FET (OCMFET), with its versatility, its convenient structure (which allow keeping the organic semiconductor and the sensing area separated), and its ability to be operated without an external reference electrode.

The solution-gated organic field effect transistor (SGOFET)

This category includes Electrolyte-Gated OFETs (EGOFET) and the graphene Solution-Gated FETs (gSGFET). Although characterized by a different nature of the active material, both structures exploit the formation of an Electrical Double Layer (EDL) at the interface between the gate and the electrolyte and the active material and the electrolyte, which leads to an extremely high gate capacitance and ultra-low operating voltages. In fact, the EDL capacitance is much higher than that of the metal oxides usually employed in standard FET structures, and this fact leads to quite high transconductances. Although the structure of an SGOFET is similar to that of an OECT, the physical principles are very different. Whereas the OECT is based on a doping/dedoping of the OSC as a consequence of the application of a gate voltage, the channel of SGOFETs is virtually "impermeable" to ions: therefore, the channel carrier concentration is modulated by purely capacitive effects at the interface between the semiconductor and the electrolyte and between the gate electrode and the electrolyte, where the EDL is formed. In addition, the SGOFET has a faster response than the OECT, thanks to the nature of the EDL itself, which is able to rapidly re-arrange after a perturbation (Fahlman *et al.*, 2019).

Recently graphene, an allotrope of carbon and the most studied 2D material, has been employed as active material in liquid-gated transistors and is now widely studied for a considerable number of sensing and biosensing applications. The interest on this device has been fueled by the remarkable electrical, mechanical and chemical properties of this material, which is in fact characterized by high optical transparency, high mechanical resistance, and very high chemical stability (Wan *et al.*, 2011; Hess *et al.*, 2011a). Commonly used is also the reduced graphene oxide, which allows easier fabrication techniques with very similar electric and optical characteristics to those of chemical vapor deposited (CVD) graphene (Stankovich *et al.*, 2007; Gilje *et al.*, 2007; Tang *et al.*, 2011).

The organic charge modulated field effect transistor (OCMFET)

The OCMFET is an OFET with a peculiar double-gated structure that makes it a particularly interesting candidate for several sensing applications. In particular, this device presents an elongated floating gate, at the end of which a sensing area is fabricated by selective functionalization, and a second gate, called control gate, which is used to set the working point of the transistor. The advantage of having this second gate can be particularly useful when the device is used as a chemical sensor in that its presence makes an external reference electrode unnecessary.

The working principle of the OCMFET is straightforward: the working point is set by applying proper values of the control gate (V_{CG}) and drain (V_{DS}) voltages. In this situation, if a charge variation occurs in proximity of the sensing area, thanks to its capacitive coupling with the floating gate, it leads to a charge reorganization into the floating gate itself, which in turn determines a modulation of the carrier's density in the transistor's channel. In particular, for $V_S = 0$ V the voltage of the floating gate can be expressed as:

$$V_{FG} = \frac{C_{CG}}{C_{TOT}} V_{CG} + \frac{C_{DF}}{C_{TOT}} V_D \frac{Q_{SENSE} + Q_0}{C_{TOT}}$$

with V_D being the drain voltage, C_{CG} , C_{DF} and C_{TOT} being the control gate capacitance, the parasitic capacitance between the floating gate and the drain and the sum of all the capacitances in the structure, Q_0 the intrinsic charge possibly present in the floating gate, and Q_{SENSE} the charge capacitively coupled on the sensing area (i.e., the charge associated with the analyte to detect). If the applied voltages are kept constant, the only term that can vary during a sensing event is the last one, thus leading to a variation of the FET's threshold voltage (ΔV_{th}) that can be expressed as:

$$\Delta V_{th} = - \frac{Q_{SENSE}}{C_{TOT}}$$

In principle, this device could thus sense all those physical, chemical or biological processes that result in a charge variation onto the sensing area.

All these organic structures present several interesting properties that can be exploited in sensing and biosensing.

Sensing Applications

Bioanalytical Sensors

Organic transistors have been employed for the detection of biochemical reactions employing different device structures and a variety of sensing approaches.

As previously described in OEFTs, the transduction mechanism is based on the possibility of affecting the capability of the gate of inducing the ion exchange between the electrolyte and the channel: this has been exploited for the detection of redox-active species, which can be directly sensed at the surface of the gate electrode, (Strakosas *et al.*, 2015; Zhang *et al.*, 2014) or by means of enzymatic transduction (Braendlein *et al.*, 2017). Enzyme activity sensing has been by far the most explored application for ECTs: as a matter of fact, enzymes have been also used as labels in immunoassays (Fu *et al.*, 2017). Only recently, label-free antibody-antigen interaction detection by means of ECTs has been demonstrated (Macchia *et al.*, 2018).

The original employment of OFETs as biochemical sensors can be ascribed to the work of Bartic and co-workers, who exploited the standard working principle of the Ion-Sensitive FET for pH measurement (Bartic *et al.*, 2002) and, later on, for monitoring the activity of glucose oxidase (Bartic *et al.*, 2003). Although some other examples of Ion-Sensitive OFETs have been proposed in literature, (Medina-Sánchez *et al.*, 2014) the employment of TFTs is surely related to the possibility of proposing innovative device structures and transduction strategies, in order to overcome the limitations of such a standard approach.

Electrolyte-gated Organic FETs (EGOFETs) attracted a significant interest, as they are intrinsically low voltage devices. In EGOFETs, the active layer in the transistor is directly exposed to the measurement environment. In this configuration, two sensing surfaces are available: the active layer-electrolyte interface and the gate-electrolyte interface. Two working principles can be thus considered: the modulation of the interface potential at the first interface, of the modification of the capacitive structure of the second interface.

EGOFETs have been used for the detection of enzymes (Bhatt *et al.*, 2017) and oligonucleotides, (Dong *et al.*, 2010) employing carbon-based materials as active material. Although DNA sensing has been demonstrated by means of EGOFETs, (Kergoat *et al.*, 2012b) such a device structure has been thoroughly explored for protein detection. Indeed, proteins are not directly associated to a specific charge value, and the affinity reactions (such as antigen-antibody interaction and enzymatic reactions) are not directly based on a charge modification in the receptor, thus being difficult to be directly detected by field-effect modulation. In EGOFETs, the possibility of influencing the capacitive structure of the device thanks to a modification of the bioreceptor layer made a direct detection possible. A significant contribution to this field has been given by Luisa Torsi and co-workers: they demonstrated the recognition of several molecules by modification of the capacitive coupling, (Mulla *et al.*, 2015a,b) in some cases even with large values of the ionic strength of electrolyte. This last aspect, which made EGOFETs capable to operate beyond the normal limitations related to the Debye length in solutions, (Palazzo *et al.*, 2015) is related to an increased sensitivity factor by means of the capacitive modulation.

All the previously cited approaches are based on the employment of a reference electrode in solution, which strongly limit the portability and integration of OFET-based biochemical sensors. Standard OFET bottom-gate structures have been demonstrated as effective biochemical sensors, in which the sensing environment is left electrically floating. Several examples of OFET-based devices

for DNA sensing have been proposed, directly employing the active layer as sensing element (Zhang *et al.*, 2007; Kim *et al.*, 2011). Nonetheless, this solution is detrimental for the durability of device electrical performances, as organic semiconductor steadily degrades in liquid environment: covering the semiconductor with thin insulating layer has been proposed as a solution, (Khan *et al.*, 2010) but a more effective strategy is the complete decoupling between the active and the sensing layer.

In this sense, the Organic Charge-Modulated Field-Effect Transistor (OCMFET) previously described, represents an ideal solution. As the transistor channel is not employed as sensing element, the organic semiconductor can be encapsulated to ensure a prolonged lifetime of the device.

The working principle of the OCMFET can be employed for the detection of biochemical reactions related to charge modulation or modulation in the measurement environment. This includes, for instance, DNA hybridization detection, which has been thoroughly explored (Lai *et al.*, 2013, 2016). OCMFET-based DNA sensors demonstrated world-record sensitivity and selectivity (Lai *et al.*, 2016) at high ionic strength, thanks to the intrinsic reorientation ability of bioreceptors on the floating gate (Lai *et al.*, 2015). The pH detection has been also explored by means of OCMFET-based sensors (Spanu *et al.*, 2017): thanks to the amplification ability of the OCMFET, the basic sensitivity of plasma-activated Parylene C (22 mV/pH) has been amplified to 1.4 V/pH, thus determining a super-Nernstian pH detection.

Cell Biosensors

Thanks to their advantages in terms of signal amplification and versatility, together with the intrinsic advantages that stem from the use of organic materials, organic transistor-based cellular interfaces lately gained a lot of interest among the scientific community. In fact, bioelectronic systems based on the OECT, the SGFET and the OCMFET have been studied for both *in vitro* and *in vivo* applications, becoming nowadays a valid alternative to standard devices such as microelectrode arrays (MEAs) and silicon-based transistors.

One of the first examples of *in vitro* cellular interface was reported in 2010 by Lin *et al.* (2010). In this work, the authors used an OECT device to assess the viability of two types of non electrogenic cells by culturing them on the channel of the transistor and evaluating the transfer curves before and after the administration of a toxic drug. The presence of the cellular layer induces different effects (which can be ascribed to the electrostatic interaction between the cells and the conducting polymer that constitutes the transistor's channel) on the device depending on the compactness of the layer itself, and this compactness strongly depends on their health. This first example was followed in the next years by a great number of other interesting studies aimed at the investigation of the great potentials of the OECT for *in vitro* cellular interfacing for toxicological applications (Jimison *et al.*, 2012; Tria *et al.*, 2013a,b, 2014; Rivnay *et al.*, 2015). In fact, it has been demonstrated that PEDOT:PSS OECTs can outperform state-of-the-art toxicological assays such as immunofluorescence, permeability assays, and impedance measurements, in terms of temporal resolution, sensitivity, specificity, and frequency response. Thanks to the peculiar sensitivity of OECTs, it was possible to use specifically engineered OECT arrays to discriminate between healthy and cancer cells, (Yeung *et al.*, 2019) to get unprecedented insights into the early stage of tissue formation, to dynamically monitor the tissue's health condition, (Ramuz *et al.*, 2015) and to detect cancer protein biomarkers both in lysated and living cells (Fu *et al.*, 2017). Another interesting application that has been tackled recently, is the use of OECT devices to study the characteristics of tridimensional cellular aggregates (Curto *et al.*, 2018). The transition from standard "planar" and 3D cellular cultures is in fact a fast growing branch of the *in vitro* practise, which can lead to a better understanding of cellular physiology while maintaining the advantages of the *in vitro* experimentation over the *in vivo* one. The use of innovative OECT structures such as the tubistor (Pitsalidis *et al.*, 2018) allowed the reliable real time monitoring of cell attachment and growth onto a 3D scaffold from the early stage to the complete development of the tissue. OECT-based sensors can be also employed for the monitoring of electrogenic cell cultures *in vitro*, (both planar and 3D), (Yao *et al.*, 2015; Gu *et al.*, 2016, 2019; Hempel *et al.*, 2017; Liang *et al.*, 2018) with excellent results in terms of signal-to-noise-ratio, sensitivity, and stability.

The interesting characteristics (such as biocompatibility, high-sensitivity, and optical transparency) of the PEDOT:PSS OECTs have been also exploited for *in vivo* cellular interfacing, in particular for electrocorticographic applications, (Khodagholy *et al.*, 2013; Lee *et al.*, 2017) obtaining higher SNR if compared to passive planar electrodes, and similar features to those typically obtained using penetrating electrodes. The versatility of the OECT has been exploited also for the detection *in vivo* of several molecules such as glutamate, acetylcholine or dopamine with high selectivity, (Kergoat *et al.*, 2014; Gualandi *et al.*, 2016; Wang *et al.*, 2017; Xie *et al.*, 2020) thus ultimately demonstrating the great potentials of this device for *in vivo* cellular interfacing.

The application of SGOFETs for cellular studies have been mainly limited to the study of electrogenic cells, and the most studied solution-gated device is undoubtedly the graphene transistors (gSGFET), thanks to the impressive properties of graphene, such as chemical stability and very high mobility. After the first example proposed by Cohen-Karni *et al.* (2010) different implementations of the gSGFET concept have been successfully studied, (Hess *et al.*, 2011b; Balandin, 2013) with very interesting results in terms of transconductance, signal-to-noise-ratio (due to a very low 1/f noise), and stability in aqueous solutions. The extremely high performances of gSGFET can be exploited for the detection of the activity of single voltage-gated ion channels, (Hess *et al.*, 2015; Seifert *et al.*, 2015) an achievement impossible to obtain using standard MEAs and silicon based field effect devices. In addition to the high stability and sensitivity of graphene FETs, the device optical transparency and the possibility of fabricating these devices onto flexible substrates are also important aspects when dealing with cellular interfaces (Kireev *et al.*, 2016; Veliev *et al.*, 2017).

The use of graphene transistors for *in vivo* applications has been vastly investigated during the past 10–15 years. In fact, the very important features of flexibility, optical transparency and excellent electronic performance, have been exploited for both

electrocorticography and high resolution epicortical and intracortical mapping of brain activity (Hébert *et al.*, 2018; Masvidal-Codina *et al.*, 2019). Particularly outstanding, as previously mentioned, is the low frequency performance of graphene-based devices, which makes these tools extremely useful in the thorough analysis of the brain activity *in vivo*.

The use of OCMFETs as a cellular interface has been proposed in 2013, (Demelas *et al.*, 2013) while the first working example has been reported soon after (Spanu *et al.*, 2013). The main feature offered by this device is the possibility of sensing a variety of different chemical/physical parameters, due to the extreme versatility of its transduction principle. In 2015, the so-called MOA (Multi OCMFET Array) was presented as a convenient tool for neuropharmacology and validated with both rat cardiomyocytes and rat primary neuronal cultures, (Spanu *et al.*, 2015) with promising results in terms of signal-to noise-ratio and stability. Interestingly, the same device can be used as a cellular metabolic sensor thanks to the possibility of turning the OCMFET to an ultra-sensitive pH sensor using a simple physical functionalization of the sensing area (Spanu *et al.*, 2018). These examples demonstrate the intriguing potentials of such device for the realization of multi-sensing systems for cellular applications.

Physical Sensors

Efficient sensors for physical parameters may be fabricated starting from the concept of organic Field Effect Transistors (OFETs).

For instance, several examples of pressure and strain sensors based on OFETs have been reported recently. Some approaches are based on capacitive changes in the gate dielectric, as recently reported by Bao's group (Mannsfield *et al.*, 2010): microstructuring the framework of an elastomeric material as dielectric layer of a capacitor, it is possible to increase the sensitivity in terms of $\Delta C/C_0$, being C_0 the pristine capacitance value. Zhenan Bao's group was the first to report a microstructured PDMS layer as a gate dielectric in a FET structure. In a first work, presented in 2010, a single-crystal Rubrene semiconductor and a layer of PDMS pillars as gate dielectric were employed. The sensor shows a very high sensitivity, large working pressure range [0.2–18 kPa], and negligible hysteresis (Someya *et al.*, 2004).

Pressure and strain sensors can be also fabricated, as reported in (Cosseddu *et al.*, 2013, 2012), by exploiting the mobility changes induced by local morphological deformations that take place in the active layer of flexible transistors when a mechanical stress, vertical or lateral, is applied. As an example, it has been recently demonstrated that by applying a compressive or tensile strain in Pentacene based organic field effect transistor, a reproducible variation of the device output current can be obtained (Trung *et al.*, 2014).

A similar approach can be also employed for the fabrication of temperature sensors. In fact, as hopping transport is strongly dominated by temperature variations, several authors have reported about the fabrication of temperature sensors using different kinds of organic semiconducting materials as active layer, and a reproducible current variation induced by temperature was demonstrated.

As an example, Graz *et al.* recently proposed a FET-based temperature sensor, with a high thermal responsivity (Graz *et al.*, 2009). The device exploits the thermosensitive property of a nanocomposite layer of reduced graphene oxide (R-GO) and a pyroelectric polymer (PVDF-TrFE). The device shows a very high resolution ($\sim 0.1^\circ\text{C}$) which is comparable to that of human skin, and a very large range of detectable temperatures [30–80°C].

Another possible strategy to obtain highly sensitive and specific physical sensors is integrating OFET devices with a piezo(pyro)resistive or piezo(pyro)electric materials. Someya *et al.* very recently demonstrated that by connecting a piezoresistive sensor in series with the drain of an organic transistor, highly sensitive devices can be fabricated (Someya *et al.*, 2004).

A different approach has been developed by Bonfiglio's group and is based on the OCMFET concept previously described. For physical sensing purposes, the sensing area of the OCMFET can be functionalized with some pressure or temperature sensitive material, as for instance a piezo(pyro)electric polymer. In this case, the applied pressure or the temperature variation induce a charge separation in the polymer, thus leading to a charge redistribution in the transistor floating gate. The authors have recently demonstrated that by using such approach, highly sensitive, multimodal sensors, capable to detect at the same time pressure and temperature variations, can be obtained (Spanu, 2016; Viola *et al.*, 2018).

Future Directions

Organic bioelectronic sensors are a rapidly expanding field of research. Starting from the successful examples of applications shown in this article, the scientific community is appreciating the huge potential of organic materials in fabricating sensing devices endowed with mechanical, chemical, physical properties very similar to those of biomolecules and cells, thus allowing a seamless integration with any bio-environment. Engineering these interfaces to make them able to fulfill an almost infinite variety of sensing tasks is the challenge for the future of this technology, whose remarkable advantage is also that of easily adapting to the whole dimensional scale of interest for biology, from the single biomolecule, to cells, organs and the whole body. Several fields of applications have already approached this technological front: drug testing, toxicology, environmental analytics, electrophysiology, genomics, proteomics, cell biology, biomonitoring systems for the whole human body are among those that will mostly benefit from the development of this versatile and intrinsically low cost technology.

Conclusions

We have here described the basic principles of organic electronic biosensors. Starting from the basic structures of organic transistors, we have shown how they can be easily adapted to a variety of sensing tasks, both for chemical and physical sensing.

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Preface

DaeYong Jeong, Department of Materials Science and Engineering, Inha University, Incheon, Republic of Korea

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The science and technology of functional materials are progressing fast and expanding in many new directions of application and processing methods. These expanding new applications and technologies, as well as the reconsideration of old processes, initiated the publication of the “Encyclopedia of Materials: Electroceramics” for interaction between scientists and engineers interested in electroceramics.

The “**Encyclopedia of Materials: Electroceramics**” has offered a compilation of some of the latest and finest research works on the materials and devices applications describing fundamentals, design, fabrication, characterization, and applications of electroceramics. The section contains 13 chapters with the following exciting subjects – **Ferroelectric Devices, Ferroelectric Memory, Ferroelectric Ceramic-Polymer Nanocomposites for Energy Storage, High-Power Piezoelectric Materials, Lead-free Piezoelectric Ceramics, Piezoelectric Ultrasonic Power Transducers, Piezoelectric Energy Harvesting, Magnetoelectric Composite Thick and Thin Films, Flexo-properties in Ceramics, Electrocaloric Ceramics, Thermoelectric Materials, Metal Oxide Ceramic Gas Sensors, Perovskite Solar Cell.**

The painstaking preparation of this voluminous work has been made possible only because of the enormous cooperation and support that I received from the authors who have graciously contributed their priceless chapters to this encyclopedia. I do express my utmost thanks and gratitude to all of them. It would be my most excellent satisfaction if these chapters turn out to be fruitful and are of academic benefit to the researchers working on electroceramics. I am indebted to Professor A S M A Haseeb, the Editor-in-Chief of the encyclopedia, for providing me with the generous offer of this editorial assignment as well as for his constant cooperation. A special expression of gratitude is extended to the staff members at Elsevier. Without their assistance, it would be impossible to publish this book.

Finally, we hope every reader can enjoy this book.

Electrocaloric Ceramics

Sedat Alkoy, Department of Materials Science and Engineering, Gebze Technical University, Gebze, Kocaeli, Turkey

MB Okatan, Department of Materials Science and Engineering, Izmir Institute of Technology, Izmir, Turkey

IB Misirlioğlu, Faculty of Natural Sciences and Engineering, Sabanci University, Istanbul, Turkey

Ebru Menşur-Alkoy, Department of Materials Science and Engineering, Gebze Technical University, Gebze, Kocaeli, Turkey

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Abstract

Electrocaloric effect (ECE) is a coupling between thermal and electrical phenomena, specifically it is the change in the entropy of a dielectric material as a result of an electrical stimulus. Electrocaloric materials are currently being investigated as a solid state refrigeration approach for on-chip cooling applications. Among the organic and inorganic electrocaloric material choices, electrocaloric ceramics are at the forefront with their higher electrocaloric coefficients. This article gives a background on the fundamentals of electrocalorics and then discusses the general trends in the literature on the electrocaloric ceramics research.

Introduction

Electronic circuits and devices working in extreme environments require compact, efficient, and environmentally friendly systems and materials for on-chip or on-board micro-cooling applications and energy storage, as such systems can be expected to operate in a large temperature range. Conventional cooling (refrigeration) technologies use gas as the coolant and pressure to induce a change in the state of the coolant. The refrigeration is obtained through the compression and expansion cycles of the gas where the entropy change in the gas each time the gas expands is the agent to remove heat from the medium via entropy transfer. Although this technology is the most commonly used one in conventional refrigeration and its coefficient of performance ($COP = \text{output cooling power}/\text{input power}$) is high, the components are rather bulky and not suitable for miniaturization. Alternative cooling technologies include thermoelectrics, magnetocalorics, and electrocalorics, the so-called “solid-state refrigeration” systems.

They utilize three principles:

- **Thermoelectric Effect (TEE):** Inducing a temperature change by running a current through a junction of two different materials. TE is suitable for miniaturization and micro cooling applications, such as CCD chip coolers, but they are prone to low efficiency due to the Joule heating due to resistive losses. In fact, the COP of TE cooling devices is usually less than 0.3.
- **Magnetocaloric Effect (MCE):** A coupling between thermal and magnetic properties where a paramagnetic material magnetized under isothermal conditions is demagnetized under adiabatic conditions through the removal of the magnetic field. The material cools due to the change in the entropy as the magnetic dipoles return to their disordered state via entropy transfer from the lattice to the magnetic spins. The COP of magnetocalorics is around 7–10.
- **Electrocaloric Effect (ECE):** ECE is an electric field induced temperature and/or entropy change in an insulating material. Application of an external electric field under adiabatic conditions induces a preferable orientation of dipoles along the field direction, decreasing the entropy, which in return leads to an increase in temperature. Reversibly, adiabatic depolarization after the removal external electric field results in the return of the electrical dipoles to their initial disordered state, leading to an increase in the entropy of the system and a resultant cooling (**Fig. 1**).

Since it is much simpler to achieve high electrical fields compared to the magnetic fields, ECE allows the possibility for a variety of applications and miniaturization through compact devices with simple geometries. The EC devices with potential COP values of 7–10 can possibly be developed for cooling applications in microrobotics and microelectronics such as microchips working in harsh environments that are faced in aviation and space exploration (Alpay *et al.*, 2014; Kutnjak *et al.*, 2015).

Background/Fundamentals

ECE was first observed in Rochelle salt in 1930 (Kobenko and Kurtschatov, 1930) and was studied further experimentally and theoretically in various dielectric materials (Lang, 1976; Lawless, 1993). For several decades, the ECE was mostly of theoretical and scientific interest due to the minute levels of the EC response, i.e., the change in temperature T (ΔT) that was observed as a result of the application of an external electric field (ΔE). However, observation of a “giant ECE”, i.e., temperature changes exceeding 10°C in ferroelectric thin films as a result of the application of voltages of only several volts created a surge of interest in electrocalorics (Mischenko *et al.*, 2006; Lu *et al.*, 2010). As of 2022, a search of published scientific literature in the Web of Knowledge database using the “electrocaloric” keyword yields a list of over 1300 papers and further narrowing the search to “electrocaloric ceramics”, which is the topic of the current work, still yields a list of over 500 published work with only 20 of them published before 2006.

The ease of application of an electric field to induce the temperature change allows designing devices with compact and simple geometries compatible with many applications requiring thermal management (Fulanovic *et al.*, 2017). Additionally, considering the bottlenecks that the society faces in terms of generation and efficient consumption of energy as well as the environmental

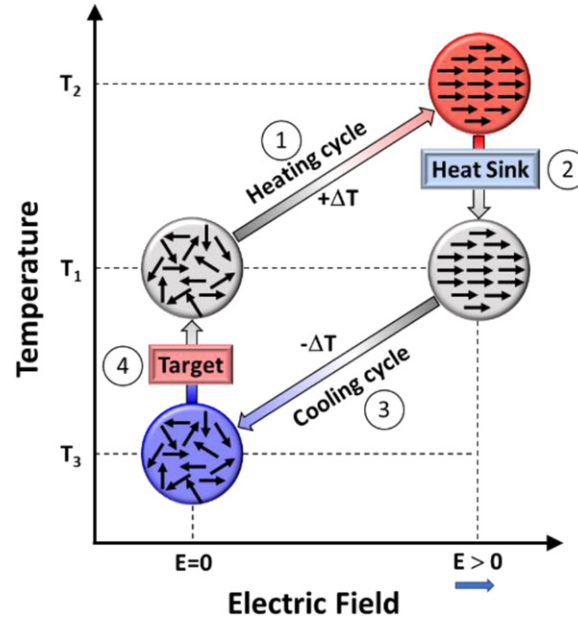


Fig. 1 Schematic representation of the change in the polar states and the temperature during the electrocaloric cycle.

concerns that have risen due to the global warming, solid state cooling approaches such as ECE could be exploited in refrigeration as a substitute for, or as an extension of, conventionally employed vapor-compression systems, especially in miniature, on-board cooling systems. A high efficiency, an absence of harmful refrigerants or bulky mechanical/magnetic parts, and a low noise would be the most obvious advantages of possible EC devices. Thus, the search continues for organic or inorganic electrocaloric materials with: (1) high ΔT values that can be obtained (2) under reasonable electric fields, i.e., higher $\Delta T/\Delta E$ ratios, and (3) with creative device topologies to allow efficient removal of the heat from the target.

Before discussing the specific ceramic systems that have been investigated for their ECE performance, a theoretical background is given to provide a general understanding of the ECE. First, consider the Gibbs free energy of a crystal that is given by the relation

$$dG = Vdp - SdT + DdE \quad (1)$$

that represents an infinitesimal change in free energy in response to changes in pressure p , temperature T and electric field E . All the product terms above are conjugated parameters for the thermodynamic system under consideration. V is the molar volume, S is the molar entropy, D is the total dielectric displacement. If one fixes pressure p , which is mostly the case in applications, the first term in Eq. 1 becomes zero and from the coefficient relations in Eq. 1, one can realize that

$$\left(\frac{dS}{dE}\right)_T = -\left(\frac{dD}{dT}\right)_E \quad (2)$$

that relates the change in entropy of the system with an electric field to the change in dielectric displacement with temperature. In a ferroelectric, dielectric displacement is almost equal to polarization and thus

$$\left(\frac{dS}{dE}\right)_T = -\left(\frac{dP}{dT}\right)_E \quad (3)$$

The left-hand side term in Eq. 3 is not directly accessible by experiment but the latter is just the pyroelectric response of the ferroelectric. The pyroelectric response is obtainable from the relation between the polarization and electric field via the Landau-Ginzburg equation of state. Another condition imposed on the system is that the system remains under adiabatic conditions, i. e., the system has no means of entropy (and therefore heat) exchange with the surroundings during the application of the electric field. While this is an ideal assumption, it is necessary for consistent thermodynamic treatment and yields rather well results in comparison to experimental observations. The condition of adiabaticity requires that

$$dS = \left(\frac{dS}{dT}\right)_E dT + \left(\frac{dS}{dE}\right)_T dE = 0 \quad (4)$$

and using the previously written coefficient relations, the above condition can now be written as

$$dS = \left(\frac{dS}{dT}\right)_E dT + \left(\frac{dP}{dT}\right)_E dE = 0 \quad (5)$$

which, upon some algebra, can be brought to the form

$$\frac{dT}{dE} = \frac{T}{C_E} \left(\frac{dP}{dT} \right)_E \quad (6)$$

where C_E is the heat capacity of the material at a constant electric field, dP/dT term is the pyroelectric coefficient at the constant electric field. To find the change in temperature of the ferroelectric upon the change of electric field from an initial value E_i to a final one E_f , one needs to integrate the right-hand side of Eq. 6 within the boundaries of interest and one can thus write

$$\Delta T = \int_{E_i}^{E_f} \frac{T}{C_E} \left(\frac{dP}{dT} \right)_E dE \quad (7)$$

Through this final relationship, the pyroelectric coefficient can be determined using a portion of the upper branch of P vs E hysteresis loops for which $E \geq 0$ kV/cm. The derivative of P vs T data at constant E , i.e., the pyroelectric coefficient, can be calculated in two different ways: (1) from the fourth order polynomial fits and (2) from finite differences on a linear interpolator. This is known as the *indirect method* to determine the electrocaloric effect. However, care should be taken in its usage, especially in relaxor ferroelectric systems, and the results should be verified through electrocaloric thermometry, the so-called *direct method* (Kutnjak et al. 2015).

Electrocaloric Ceramics

Thin and Thick Ceramic Films

Although studies on electrocaloric effect have a history of a century, the majority of the studies were conducted within the last 15 years and accelerated after the report by Mischenko et al. (2006) on the observation of a giant temperature change of 12K in $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ thin films. Due to the inherent higher electric breakdown strength (E_b) of thin films, it becomes possible to achieve rather very high electric field levels ($\Delta E > 100$ kV/cm) simply by applying bias voltages of only several volts. Thus, EC materials in thin film form allow achieving temperature changes amounting to several degrees, exceeding 10°C in some rare cases (Saranya et al., 2009; Lu et al., 2010; Peng et al., 2013). A non-exhaustive list of several electrocaloric ceramics in thin and thick film form is given in Table 1.

The presence of a substrate in a thin film structure may lead to misfit strain due to lattice mismatch at the interfaces and/or the different thermal expansion coefficient between the film and the substrate. These misfit strains can be engineered to enhance or tune certain properties, as it was theoretically investigated by Li et al. (2014), where anisotropic in-plane strains on the EC response of PbTiO_3 (PT) epitaxial ferroelectric thin films was investigated using a Landau-Devonshire thermodynamic theory. In that study ΔT values surpassing 10K were calculated to be possible as a result of misfit strains. A theoretical study conducted by Hou et al. (2018) using a phase field approach on the effect of misfit strains on the ECE of PT indicated that a giant negative ECE could be expected in the strained PT thin film is induced by domain transition at a temperature below the Curie temperature. It was also calculated that the maximum negative ECE and the temperature at which it occurs can be tuned by the magnitude of the mismatch strain as strain can profoundly impact the ferroelectric-paraelectric transition temperatures (Pertsev et al., 1988). As the pyroelectric coefficient reaches a maximal value near the transition temperature, the ECE is also expected to enhance at the transition as can be seen in Eq. 7. Pandya et al. (2018) conducted an experimental study with $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films to investigate the role of ferroelastic domains on the pyroelectric and electrocaloric effects. They used the epitaxial strain to modify the ferroelastic domain structure of the films and concluded that the field-dependent change in the ferroelastic domains results in an inverse caloric effect

Table 1 Electrocaloric ceramics in thin and thick film form

Composition	ΔT (K)	$\Delta T/\Delta E$ (Km/V)	T_{EC} ($^\circ\text{C}$)	Meas. Method	References
Thin Films					
$\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$	12	2.5×10^{-7}	226	Indirect	(Mischenko et al., 2006)
$0.65 \text{ Pb}(\text{Mg}1/3\text{Nb}2/3)\text{O}_3 - 0.35 \text{ PbTiO}_3$	31	4.1×10^{-7}	140	Indirect	(Saranya et al., 2009)
$0.93 \text{ Pb}(\text{Mg}1/3\text{Nb}2/3)\text{O}_3 - 0.07 \text{ PbTiO}_3$	9	1.2×10^{-7}	25	Indirect	(Correia et al., 2009)
$\text{SrBi}_2\text{Ta}_2\text{O}_9$	4.93	0.82×10^{-7}	288	Indirect	(Chen et al., 2009)
$(\text{Pb}_{0.88}\text{La}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$	40	3.3×10^{-7}	45	Direct	(Lu et al., 2010)
$(\text{Pb}_{0.8}\text{Ba}_{0.2})\text{ZrO}_3$	45.3	7.6×10^{-7}	20	Indirect	(Peng et al., 2013)
$(\text{Ba}_{0.3}\text{Sr}_{0.7})\text{TiO}_3$	1.5	0.3×10^{-7}	RT	Indirect	(Yamada et al., 2017)
Thick Films					
$0.65 \text{ Pb}(\text{Mg}1/3\text{Nb}2/3)\text{O}_3 - 0.35 \text{ PbTiO}_3$	2	2.5×10^{-7}	154	Direct	Rožič et al., 2012
$0.70 \text{ Pb}(\text{Mg}1/3\text{Nb}2/3)\text{O}_3 - 0.30 \text{ PbTiO}_3$	1.2	1.0×10^{-7}	107	Direct	Rožič et al., 2014
$(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.73}\text{Sn}_{0.22}\text{Ti}_{0.05})\text{O}_3$	(111) 28.1	3.3×10^{-7}	21	Indirect	(Zhao et al., 2016)
	(110) 23.1	2.6×10^{-7}			
	(100) 21.2	2.4×10^{-7}			
$\text{Pb}_{0.82}\text{Ba}_{0.08}\text{La}_{0.10}(\text{Zr}_{0.90}\text{Ti}_{0.10})\text{O}_3$	25.1	3.6×10^{-7}	RT	Indirect	(Gao et al., 2017)

T_{EC} is the temperature at which the maximum ECE response was reported.

in the compressive strain regime and in a conventional, i.e., positive caloric effect in the tensile strain regime. Thus, epitaxial misfit strains in thin films were experimentally demonstrated to be a viable way to enhance the electrothermal behavior of the films.

One restriction for thin films, however, emanates from the very definition of the system: a thin film volume often has an extremely small thermal mass to effectively remove heat from the system to be thermally managed despite the attractive temperature changes these systems can possess under bias. A compromise would be to use thick films ($t > 1 \mu\text{m}$), where the E_b is still high, the drive voltages are still reasonable and thermal mass is relatively higher than thin film structure (Zhao *et al.*, 2016; Gao *et al.*, 2017).

The thin and thick film structures also allow one to access the crystal anisotropy through epitaxial growth of the films along various crystallographic directions. The study conducted by Zhao *et al.* (2016) on $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.73}\text{Sn}_{0.22}\text{Ti}_{0.05})\text{O}_3$ films grown with $\langle 111 \rangle$, $\langle 110 \rangle$ or $\langle 100 \rangle$ directions of the perovskite structure indicates a clear variation of the ECE with film epitaxy, as given in Table 1. This variation was attributed to the preferable orientation of the spontaneous polarization directions in the corresponding antiferroelectric and ferroelectric phases with respect to the crystallographic orientation of the films.

Bulk Ceramics

Although thin films may display ΔT values easily surpassing several degrees with very low driving voltages, their inherent restrictions, such as the limited thermal mass for effective cooling, require investigation of bulk ceramics for practical device applications. In the identification of promising bulk ceramic compositions for large EC response, materials with large entropy changes should be studied. The highest response is usually observed in ferroelectric materials around the ferroelectric-paraelectric phase transitions (Mischenko *et al.*, 2006) and especially at temperatures slightly above the Curie temperature. Additionally, the latent heat related to a field induced transition between antiferroelectric to ferroelectric phases was also cited to contribute to the ECE response of such materials below the depolarization temperature T_{dp} , leading to a giant ECE response (Peng *et al.*, 2013). Large ECE response can also be expected in materials with invariant critical point (ICP) where a multiple number of phases coexist and phase changes can be induced relatively easily through applied electric fields, as theoretically discussed by Liu *et al.* (2012) and experimentally demonstrated in the Zr modified BaTiO_3 relaxor ceramics by Qian *et al.* (2014). The polar nanoregions (PNRs) in the relaxor systems and their effect on ECE have also attracted research interest in recent years, since PNRs were claimed to enhance the ECE through possession of multiple orientation possibilities, which can be acted upon by an external field (Lu *et al.*, 2010; Li *et al.*, 2019). Due to their diffuse phase transition compared to the normal ferroelectrics, the relaxors provide the added benefit of a wider range of operational temperatures for practical EC device applications. The intentional creation of point defects in lead zirconate titanate through La doping to disturb the long-range polar order in a normal ferroelectric and induce a relaxor-like behavior was also investigated by Gözüağık *et al.* (2022), where the local electric fields created through the dipolar defect complexes that arose in the structure led to a smearing of the phase transition, as well as increase EC response.

Thus, studies on the bulk electrocaloric ceramics in the literature can be divided into several sub-groups such as normal ferroelectrics, relaxor ferroelectrics, antiferroelectrics, and materials with critical compositions where several of these phases co-exist and where phase transitions can readily be induced through the application of electric fields. In all these various materials, both lead-free and lead-based ferroelectric compositions have been investigated with the lead-free materials leading the research effort

Table 2 Lead-based electrocaloric ceramics in bulk form

Composition	ΔT (K)	$\Delta T/\Delta E$ (Km/V)	T_{ec} ($^{\circ}\text{C}$)	Meas. Method	Reference
$\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.75}\text{Sn}_{0.20}\text{Ti}_{0.05})\text{O}_3$	2.60	8.67×10^{-7}	161	Direct	(Tuttle and Payne, 1981)
$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	2.50	2.77×10^{-7}	47	Direct	(Rožič <i>et al.</i> , 2011a)
$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	2.50	2.77×10^{-7}	16	Direct	(Rožič <i>et al.</i> , 2011b)
0.92 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.08 PbTiO_3	0.58	11.60×10^{-7}	30	Direct	(Molin <i>et al.</i> , 2015)
0.90 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.10 PbTiO_3	3.45	2.16×10^{-7}	127	Direct	(Vrabelj <i>et al.</i> , 2016)
0.90 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.10 PbTiO_3	1.50	1.30×10^{-7}	RT	Direct	(Plaznik <i>et al.</i> , 2015)
0.87 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.13 PbTiO_3	0.56	2.32×10^{-7}	70	Direct	(Hagberg <i>et al.</i> , 2008)
0.85 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.15 PbTiO_3	1.71	10.68×10^{-7}	18	Direct	(Shaobo and Yanqiu, 2004)
0.75 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.25 PbTiO_3	2.10	3.81×10^{-7}	25	Indirect	(Kriak <i>et al.</i> , 2015)
0.70 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.30 PbTiO_3	2.80	3.11×10^{-7}	157	Direct	(Rožič <i>et al.</i> , 2011a)
0.70 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.30 PbTiO_3	1.55	3.10×10^{-7}	170	Direct	(Peräntie <i>et al.</i> , 2013)
0.70 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.30 PbTiO_3	1.27	2.17×10^{-7}	107	Direct	(Uršič <i>et al.</i> , 2016)
0.85 $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - 0.15 PbTiO_3	0.37	2.01×10^{-7}	225	Indirect	(Ramesh <i>et al.</i> , 2016)
0.64 $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ - 0.36 PbTiO_3	0.63	1.56×10^{-7}	260	Indirect	(Qiao <i>et al.</i> , 2018)
$(\text{Pb}_{0.88}\text{La}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$	2.25	2.56×10^{-7}	110	Direct	(Rožič <i>et al.</i> , 2011a)
$(\text{Pb}_{0.88}\text{La}_{0.08})(\text{Zr}_{0.70}\text{Ti}_{0.30})\text{O}_3$	1.15	2.55×10^{-7}	20–80	Indirect	(Gözüağık <i>et al.</i> , 2022)
$(\text{Pb}_{0.91}\text{La}_{0.06})(\text{Zr}_{0.80}\text{Ti}_{0.20})\text{O}_3$	0.98	2.45×10^{-7}	140	Direct	(Li <i>et al.</i> , 2019)
$\text{Pb}_{0.35}\text{Sr}_{0.65}\text{TiO}_3$	2.05	5.12×10^{-7}	50	Direct	(Ge <i>et al.</i> , 2019)
$\text{Pb}_{0.3}\text{Ca}_{0.05}\text{Sr}_{0.65}\text{TiO}_3$	1.71	2.14×10^{-7}	20	Indirect	(Han <i>et al.</i> , 2019)
$\text{PbMg}_{0.5}\text{W}_{0.5}\text{O}_3$	1.79	1.49×10^{-7}	36	Direct	(Li <i>et al.</i> , 2021)
	-2.02	-2.42×10^{-7}	34		

Table 3 Lead-free electrocaloric ceramics in bulk form

Composition	ΔT (K)	$\Delta T/\Delta E$ (K/mV)	T_{ec} ($^{\circ}$ C)	Meas. Method	Reference
0.94(Na _{1/2} Bi _{1/2})TiO ₃ - 0.06BaTiO ₃	1.50	3.00×10^{-7}	100	Indirect	(Cao et al., 2014)
0.94(Na _{1/2} Bi _{1/2})TiO ₃ - 0.06BaTiO ₃	-2.61	5.22×10^{-7}	64	Indirect	(Li et al., 2016a)
0.98BaTiO ₃ - 0.02(BiMg _{1/2} Ti _{1/2})O ₃	1.21	2.30×10^{-7}	143	Indirect	(Li et al., 2018a)
Bi _{1/2} (Na,K) _{1/2} TiO ₃	1.85	3.70×10^{-7}	32	Indirect	(Fan et al., 2017)
Bi _{1/2} (Na _{0.8} K _{0.2}) _{1/2} TiO ₃	1.08	2.16×10^{-7}	107	Indirect	(Wang et al., 2019)
{[Bi _{0.5} (Na _{0.72} K _{0.18} Li _{0.1}) _{0.5}] _{0.98} Sr _{0.02} }TiO ₃	2.51	3.86×10^{-7}	85	Indirect	(Zhang et al., 2020)
0.85 K _{0.5} Na _{0.5} NbO ₃ - 0.15SrTiO ₃	1.90	1.19×10^{-7}	67	Direct	(Koruzza et al., 2015)
BaTiO ₃	1.25	6.25×10^{-7}	130	Direct	(Novak et al., 2021)
BaTiO ₃	0.57	4.75×10^{-7}	135	Indirect	(Gwizd et al., 2021)
Ba _{0.65} Sr _{0.35} TiO ₃	1.82	6.07×10^{-7}	RT	Direct	(Dai et al., 2020)
Ba _{0.67} Sr _{0.33} TiO ₃	2.63	2.39×10^{-7}	25	Indirect	(Xu and Qiang, 2017)
Ba _{0.70} Sr _{0.30} TiO ₃	1.92	3.84×10^{-7}	42	Indirect	(Wang et al., 2022)
Ba _{0.96} La _{0.04} TiO ₃	1.81	3.02×10^{-7}	30	Indirect	(Lv et al., 2020)
Ba _{0.94} Dy _{0.04} TiO ₃	1.04	3.47×10^{-7}	138	Indirect	(Han et al., 2016)
Ba _{0.7} Sr _{0.3} Ti _{0.99} Mn _{0.003} O ₃	2.53	2.11×10^{-7}	30	Indirect	(Liu et al., 2014)
Ba _{0.995} Ca _{0.005} Ti _{0.99} Mn _{0.01} O ₃	1.22	4.07×10^{-7}	120	Indirect	(Liu et al., 2018)
Ba(Zr _{0.2} Ti _{0.8})O ₃	4.50	3.10×10^{-7}	39	Direct	(Qian et al., 2014)
Ba(Zr _{0.2} Ti _{0.8})O ₃	2.78	1.73×10^{-7}	80	Indirect	(Zhang, 2018)
BaHf _{0.11} Ti _{0.89} O ₃	1.35	2.70×10^{-7}	65	Indirect	(Li et al., 2016b)
BaTi _{0.85} Sn _{0.15} O ₃	1.49	4.97×10^{-7}	26	Direct	(Li et al., 2018b)
BaTi _{0.91} Sn _{0.09} O ₃	0.47	1.57×10^{-7}	54	Indirect	(Kacem et al., 2021)
Ba _{0.85} Ca _{0.15} (Zr _{0.1} Ti _{0.89} Fe _{0.01})O ₃	0.86	2.32×10^{-7}	72	Indirect	(Patel et al., 2015)
(Ba _{0.95} Ca _{0.05}) _{0.8875} Bi _{0.075} TiO ₃	0.81	2.05×10^{-7}	84	Indirect	(Zaghoulene et al., 2018)
Ba _{0.85} Sr _{0.15} Ti _{0.9} Zr _{0.1} O ₃	2.40	6.49×10^{-7}	30	Indirect	(Patel et al., 2016)
Ba _{0.8} Ca _{0.2} Ti _{0.96} Zr _{0.04} O ₃	0.27	3.40×10^{-7}	107	Indirect	(Asbani et al., 2016)
Ba _{0.9} Ca _{0.1} Ti _{0.95} Zr _{0.05} O ₃	1.64	2.34×10^{-7}	130	Indirect	(Nie et al., 2017)
Ba _{0.9} Ca _{0.1} Ti _{0.95} Zr _{0.05} O ₃	0.57	1.88×10^{-7}	119	Indirect	(Abdessalem et al., 2018)
SrBi _{1.85} Pr _{0.15} (Nb _{0.2} Ta _{0.8} hO ₉	0.46	0.84×10^{-7}	150	Direct	(Axelsson et al., 2017)
SrBi ₂ (Nb,Ta) ₂ O ₉	0.78	1.56×10^{-7}	140	Direct	(Axelsson et al., 2018)
(Sr _{0.75} Ba _{0.25})Nb ₂ O ₆	0.30	1.00×10^{-7}	164	Indirect	(Singh et al., 2016)

by far. Another important parameter that needs to be considered in selecting high-performance EC compositions is the requirement that the EC material should show its high EC temperature change temperature range around the temperature that the EC device will operate (Valant et al., 2012). An exemplary, non-exhaustive list of bulk electrocaloric ceramics and their primary ECE properties are presented in Table 2 for lead-based and Table 3 for lead-free bulk electrocaloric ceramics.

Several conclusions can be drawn from these tables:

Relatively higher ΔT values surpassing 1K can be obtained from bulk ceramics with modest applied electric fields due to their high EC coefficients ($\Delta T/\Delta E$). But the EC coefficients of the majority of the ceramics are less than 5×10^{-7} K•m/V. However, there is a group of bulk materials in the case of lead-free EC ceramics such as, Sr-doped BaTiO₃ (BT) compositions or BT modified (Na_{1/2}Bi_{1/2})TiO₃ (NBT) compositions that show higher EC effect, surpassing 5×10^{-7} K•m/V. Additionally, some PMN-PT and (Pb, Nb)(Zr,Sn,Ti)O₃ ceramics, in the case of lead-based compositions, were reported to achieve even higher EC coefficients around 1×10^{-6} K•m/V. These compositions require further investigation to establish a better understanding, and further development on enhancing their breakdown strength to achieve higher ΔT values.

The large ΔT values exceeding 10K reported in the literature for thin films were usually obtained with electric field levels around 500 kV/cm (Mischenko et al., 2006; Peng et al., 2013) and in some cases exceeding 1 MV/cm (Lu et al. 2010). These field levels are an order of magnitude higher than bulk ceramics and unattainable in their case due to their lower breakdown strength (Valant et al., 2012; Fulanovic et al., 2017). Even the field levels that bulk ceramics can handle such as 100 kV/cm to obtain meaningful ΔT values of > 2K for practical EC cooling devices correspond to impractical driving voltages. Additionally, heat transfer is inefficient in bulk ceramics due to the low surface-to-volume ratio and low thermal conductivity (Kar-Narayan and Mathur, 2009). Thus, EC ceramics have been investigated in a multilayer form, similar to the multilayer capacitors and piezoelectric actuators, for practical EC device applications for the last two decades (Shebanovs et al., 2002). A list of EC multilayer ceramic examples are presented in Table 4.

Single Crystals/Textured Ceramics

Electrocaloric effect is a coupling between thermal and electrical domains and can be represented as a first rank tensor property (Newnham, 2005) according to Eq. 8:

$$\Delta T = p_i \Delta E_i \quad (8)$$

Table 4 Electrocaloric ceramics in multilayer form

Composition	Layer Thick. (Hm)	# of Layers	ΔT (K)	$\Delta t/\Delta e$ (K.m/V)	T_{ec} ($^{\circ}$ C)	Meas. Method	References
PbSc _{1/2} Ta _{1/2} O ₃	64–72	16	2.40	1.74×10^{-7}	RT	Direct	(Shebanovs et al., 2002)
BaTiO ₃ ^a	6.5	200	0.50	0.17×10^{-7}	80	Direct	(Kar-Narayan and Mathur, 2010)
0.90 Pb(Mg _{1/3} Nb _{2/3})O ₃ - 0.10 PbTiO ₃	a8	49	1.20	1.17×10^{-7}	100	Indirect	(Hirose et al., 2016)
BaTiO ₃ ^a	5	180	0.9	$2.0a \times 10^{-7}$	> 120	Direct	(Lu et al., 2016)
0.90 Pb(Mg _{1/3} Nb _{2/3})O ₃ - 0.10 PbTiO ₃	60	5	230	2.26×10^{-7}	105	Direct	(Fulanovic et al., 2017)
0.92 Pb(Mg _{1/3} Nb _{2/3})O ₃ - 0.08 PbTiO ₃	a9	9	2.67	1.67×10^{-7}	80–100	Direct	(Molin et al., 2017)
0.90 Pb(Mg _{1/3} Nb _{2/3})O ₃ - 0.10 PbTiO ₃	a5-a9	19	2.70	$9.a8 \times 10^{-7}$	107	Direct	(Usui et al., 2017)
0.90 (K _{0.49} Na _{0.49} Li _{0.02})(Nb _{0.8} Ta _{0.2})O ₃ - 0.10 CaZrO ₃	20	5	2.45	0.82×10^{-7}	80	Direct	(Yang et al., 2021)
BaTiO ₃ ^a	6.5	200	0.46	0.15×10^{-7}	90	Direct	(Bsaibess et al., 2022)

^aCommercial Y5V multilayer capacitor**Table 5** Electrocaloric properties of single crystals and textured ceramics

Composition	Orientation	ΔT (K)	$\Delta T/\Delta E$ (Km/V)	T_{ec} ($^{\circ}$ C)	Meas. Method	References
Single crystals						
0.72 Pb(Mg _{1/3} Nb _{2/3})O ₃ - 0.28 PbTiO ₃	011	0.5a	5.89×10^{-7}	128	Direct	(Per�antie et al., 2010)
BaTiO ₃	–	0.90	7.50×10^{-7}	129	Direct	(Moya et al., 2013)
Sr _{0.75} Ba _{0.25} Nb ₂ O ₆	001	0.40	4.90×10^{-7}	40–80	Direct	(Le Goupil et al., 2014a)
	100	0	0			
Sr _{0.61} Ba _{0.39} Nb ₂ O ₆	001	1.10	3.92×10^{-7}	61	Direct	(Le Goupil et al., 2014b)
Pb[(Ni _{1/3} Nb _{2/3}) _{0.6} Ti _{0.4}]O ₃	100	0.76	4.50×10^{-7}	150	Indirect	(Peng et al., 2015)
NH ₄) ₂ SO ₄	001	4.50	1.13×10^{-7}	-50	Indirect	(Crossley et al., 2016)
	100	0.7a	3.65×10^{-7}			
0.76 Pb(Mg _{1/3} Nb _{2/3})O ₃ - 0.24 PbTiO ₃	110	0.79	3.95×10^{-7}	127	Indirect	(Zhang et al., 2017)
	111	0.78	3.90×10^{-7}			
Textured ceramics						
0.90 Pb(Mg _{1/3} Nb _{2/3})O ₃ - 0.10 PbTiO ₃	001	0.50	1.25×10^{-7}	50–80	Indirect	(Mensur-Alkoy et al., 2020)
	random	0.65	1.62×10^{-7}	50–80		
0.72 Pb(Mg _{1/3} Nb _{2/3})O ₃ - 0.28 PbTiO ₃	001	0.50	$0.8a \times 10^{-7}$	80	Indirect	(Bobrek et al., 2022)
	random	0.45	0.75×10^{-7}	80		

Thus, the ECE is expected to demonstrate an anisotropy in non-centrosymmetric ferroelectric crystals. However, the anisotropy of ECE has scarcely been addressed in the literature (Valant, 2012). The effect of anisotropy on the ECE was investigated in single crystals of 0.76PMN–0.24PT by Zhang et al. (2017), where distinctively different values of EC coefficients with different temperature dependent behavior were measured along the [100], [110], and [111] crystallographic directions. Sebald et al. (2006) investigated the ECE of 0.75PMN–0.25PT crystals and compared the results with random ceramics of the same composition. A clear anisotropy has again been observed in the properties with changing crystallographic direction. The effect of electrocaloric anisotropy in lead-free strontium barium niobate SBN75 (Sr_{0.75}Ba_{0.25}Nb₂O₆) based uniaxial relaxor ferroelectric single crystals with tetragonal tungsten bronze structure has also been reported by Le Goupil et al. (2014a,b).

However, it is well known that single crystals are usually considered too expensive for mass-produced device applications. Thus, a preferable approach to obtain an anisotropy in polycrystalline ceramics would be through texture development (Messing et al., 2017). There are only recent reports on the investigation of EC behavior in crystallographically textured ceramics (Mensur-Alkoy et al., 2020; Bobrek et al., 2022). In those studies, it was reported that the symmetry of the crystal, the crystallographic orientation, the direction of the applied electric field and the directions of the spontaneous polarization are the key parameters and determine whether higher ECE will be observed in a textured ceramic with respect to the random ceramic case. EC properties of single crystals and textured ceramics are given in Table 5.

Future Directions

The future directions for the electrocaloric ceramics in terms of research and progress toward device integration were addressed under several headings:

Investigation of the Secondary Contributions – Elastocaloric Effect

As ferroelectrics are piezoelectric by nature, they can also undergo volumetric changes upon application of the electric field via the converse piezoelectric coupling. Any volume change will cause a change in the temperature of the material, the so called elastocaloric effect. Whether or not this effect enhances the electric field driven temperature changes, namely the ECE, remains as another topic to be understood so that specific considerations in device design can be made (Correia and Rokosz, 2015; Li et al., 2013). A number of works have recently reported stress induced temperature changes in perovskite thin films ranging from values of 10K up to around 23K in Refs. (Liu et al., 2014b; Li et al., 2021b), bringing forth elastocaloric mechanisms as another parameter to understand in studies of caloric device design for the future.

Long Term Stability of the Electrocaloric Performance

Since an electrocaloric cooling device has to be continuously subjected to high electric fields and cycled through heating and cooling cycles, the issues of aging, fatigue (Fulanovic et al., 2017) and long-term stability (Weyland et al., 2018) of the EC performance of any candidate material should also be investigated for successful integration in a solid-state cooling device.

Effect of Anisotropy and Texture on the ECE

The anisotropy of the ECE has been addressed and demonstrated only in a few studies on single crystals (Valant, 2012; Le Goupil et al., 2014a; Zhang et al., 2017) and on textured ceramic materials (Mensur-Alkoy et al., 2020). However, further theoretical and experimental studies need to be undertaken to establish a coherent picture on all aspects of symmetry in terms of crystal orientation, polar directions and applied field direction (Okatan et al., 2022).

Electrocaloric Composites

Ferroelectric polymers were demonstrated to exhibit large ΔT values (Neese et al., 2008; Lu et al., 2010) due to their considerably higher breakdown strengths than EC ceramics. The relative ease of their processing, their conformability to large, curved surfaces, and their flexibility can be cited as advantage for possible device applications. However, the low EC coefficient ($\Delta T/\Delta E$) of polymers and the lower thermal mass of thin polymer films inhibit their widespread application for efficient solid-state cooling devices. On the other hand, the large EC coefficient and bulk form of EC ceramics are their positive aspects, whereas their lower breakdown strengths and rigidity hinder their successful implementation into devices. Thus, electrocaloric composite forms combining the best aspects of organic and inorganic EC materials, as reported by several researchers (Zhang et al., 2015a,b), seem to be one avenue that needs to be further investigated in the future.

Device Applications

As discussed and cited so far, the EC literature is rich in studies focusing on the reporting and discussing the ECE performance of electrocaloric ceramics. There are also studies further enhancing the ECE through compositional modification, such as doping (Gözüaçık et al., 2022; Patel, 2016) or invariant critical compositions (Qian et al., 2014; Zhang, 2018). Thus, the field is ready for increasing the number of innovative EC device designs, several examples of which have already been reported in the past (Ožbolt et al., 2014; Zhang et al. 2017b; Blumenthal and Raatz, 2018). These designs would possibly need to use EC ceramics in multilayer forms or electrocaloric composites with various connectivity.

Conclusions

The increasing population and disregard for the negative impacts of widespread industrialization in the last century led to global warming and associated climate change. The ever-increasing need for energy and its associated cost also requires more energy efficient air conditioning, refrigeration, and cooling devices. Modern technology using high-performance electronic circuits, batteries and miniaturized devices needs compact, on-board solid-state cooling devices. Electrocaloric ceramics are one of many critical materials being investigated for these challenging fields of application. A wide knowledge base has already been established in the last 90 years on EC ceramics, as it was partially reviewed here. However, further studies are required to develop a better understanding of the relationship of EC phenomenon with structure, phase coexistence, composition, and microstructure in the EC ceramics. Prospective directions were also identified for future studies.

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Ferroelectric Memory

Takashi Eshita, Wakayama University, Wakayama, Japan

Wensheng Wang and Yukinobu Hikosaka, Fujitsu Semiconductor Memory Solution Limited, Fukushima, Japan

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Abstract

Ferroelectric memory, including FRAM or FeRAM, FeFET and FTJ memory, is a non-volatile memory using spontaneous polarization of ferroelectrics, which have attracted much attention since the discovery of the ferroelectricity 100 years ago because it has excellent properties of high writing speed, low power consumption, and high rewriting endurance. However, it has been limited in an application because of its relatively low memory density due to inferior compatibility with the semiconductor production process. HfO₂ based ferroelectrics, which were discovered 10 years ago, have good compatibility with semiconductor process so that ferroelectric memory is expected to be a main stream of memory device in Internet of Things (IoT) era if they are proven of its high reliability.

Nomenclature

1T1C	one transistor and one capacitor
2T2C	two-transistor and two-capacitor
3D	three dimensional
ASIC	application specific integrated circuit
ASIC	application specific integrated circuit
BEOL	back end of line
BFO	BiFeO ₃
BIT	Bi ₄ Ti ₃ O ₁₂
C _b	capacitance of bit line
C _d	dielectric capacitance
C _f	capacitance of ferroelectric capacitor
CMOS	complementary metal–oxide–semiconductor.
c-phase	cubic phase
CUB	capacitors under bit line
DPGA	dynamically programmable gate array
DPGA	dynamically programmable gate array
DRAM	dynamic random access memory
E	electric field
E _c	coercive field
ECC	error correcting code
E _{depb}	depolarization field
F	feature size
FC	ferroelectric capacitor
FEOL	front end of line
FM	ferroelectric memory
FRAM or FeRAM	ferroelectric random access memory
FTJ	ferroelectric tunnel junction
HfO ₂ -Fe	HfO ₂ -based or fluorite-based ferroelectric material
LOCOS	local oxidation of silicon
MFIS	metal-ferroelectric-insulator-Si substrates
MFMS	metal-ferroelectric-metal- insulator-Si substrates
MFS	metal-ferroelectric-semiconductor
MOSFET	metal oxide semiconductor field- effect transistor
MPB	morphotropic phase boundary
NVM	non-volatile memory
o-phase	orthorhombic phase
OS	opposite state
P	polarization
P ₀	polarization in an equilibrium state
P-E	polarization-electric field
P _r	remnant polarization
P _s	spontaneous polarization

PTO	lead titanate or PbTiO_3
PVDF	polyvinylidene difluoride
PZO	lead zirconate or PbZrO_3
PZT	lead zirconate titanate or $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$
SBT	$\text{SrBi}_2\text{Ta}_2\text{O}_9$
SBTN	$\text{SrBi}_2\text{NbTaO}_9$
SRAM	static random access memory
SS	same state
STI	shallow trench isolation
T_0	phase transition temperature
T_c	Curie Temperature
TDDb	time-dependent-dielectric breakdown
t-phase	tetragonal phase
V_{dd}	externally supplied voltage

Introduction

Ferroelectric memory (FM), including ferroelectric random access memory (FRAM or FeRAM) is a non-volatile memory (NVM) which stores information as a polarization state of the ferroelectric material. Ferroelectric material has bi-stable polarization states, which are retained even in the absence of an external electric field, and can be switched between states by applying an external field. Because FM has excellent electric properties, such as a high speed read/write (< 50 ns), high switching endurance ($\geq 10^{14}$) and low power consumption in comparison with conventional NVM, such as EEPROM and FLASH memory, they have been employed by portable equipment, advanced smartcards and authentication devices so on. Although scalability has been considered as a disadvantage of FRAM for a long time because refractory noble metal needs to be used for electrodes due to the high crystallization temperature of ferroelectrics, a recent discovery of HfO_2 based ferroelectric material (Böscke *et al.*, 2011), which has been reported to be fully compatible with CMOS fabrication process thanks to its low crystallization temperature, enhances the expectation to realize an advanced memory whose memory density will be higher than that of FLASH memory even with extremely low power consumption and a high writing speed. Therefore, it has been expected to apply to various types of edge computing devices surrounding “Internet of Things (IoT)” (Eshita *et al.*, 2018). In IoT, a huge amount of data generated by various sensors is processed and optimized by edge computing before transferring to mainstream computing systems. Since edge devices, often deployed in a remote location away from the power supply, are operated by unstable self-powering processes such as an environmental energy harvesting, FM is suitable for the application to the edge devices. Other than edge computing application, FM has been proposed for various attractive applications (Mikolajick *et al.*, 2020) such as cache memories in main stream computing (Mueller, 2018), neuromorphic computing (Upadhyay *et al.*, 2019), and in-memory computing (Sebastian *et al.*, 2020; Wang *et al.*, 2020). Modern FMs are classified into almost 3 types, capacitor type FRAM, FeFET (FET type FRAM, 1 T type FRAM, or Ferroelectric memory FET: FeMFET) and ferroelectric tunnel junction (FTJ) type FMs. Along with that classification, we describe the history, memory structure, fabrication process, circuits, and recent advances in FM in this article.

Background of Ferroelectric Memory

History of Ferroelectric Memory

Ideas of storing information into ferroelectric material have already appeared in the 1950s. Pulvari (1951) proposed an idea of information storage device using ferroelectric material in 1951. The origin of the capacitor type FM goes back to the patent application by Anderson at Bell Laboratories in 1951 (Anderson, 1951 (Filling)). One year later, Buck (1952), a graduate student of MIT, described an idea of random access memory using a ferroelectric capacitor (FC) and its experimental results in his master's thesis in 1952. In the late 1980s, some start-up companies in the US began the development of practical Si-based capacitor-type FRAM with dynamic random access memory (DRAM)-like cell (Evans and Womack, 1988; Eaton *et al.*, 1988) and many electronics companies around the world started competition in the development of this type of FRAM aiming to realize a “dream memory” capable of high speed read/write and non-volatile. By the late 1990s, several US, Korea, and Japanese companies, (Nakamura *et al.*, 1995; Arita *et al.*, 1996; Yamazaki *et al.*, 1997; Jung *et al.*, 1998; Moise *et al.*, 1999) were successfully mass-producing FRAM with memory densities from 16 Kb to 256 Kb. Dimmler and Eaton proposed another capacitor type of FRAM whose memory unit is similar to that of static random access memory (SRAM), but is non-volatilized by using FCs in 1987 (Dimmler and Eaton, 1987 (filling)).

In the other hand, the origin of the FeFET goes back to a patent application by Ross at Bell Laboratories in 1955 (Ross, 1955 (filling)). Moll and Tarui (Moll and Tarui, 1963) demonstrated FeFET using Triglycine Sulfate $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$ for the first time in 1963. In 1974, Wu fabricated a FeFET using $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, which comprised a metal-ferroelectric semiconductor (MFS) gate structure (Wu, 1974). In the MFS structure, the chemical reaction between ferroelectric material and Si, which occurs during the

transistor fabrication process, degrades the transistor characteristics. To overcome this degradation, metal-ferroelectric-insulator-Si substrates (MFISs) and metal-ferroelectric-metal-insulator-Si substrates (FMFISs) (Nakamura *et al.*, 1995; Tokumitsu *et al.*, 1999; Ishiwara, 2003) were proposed. Since the discovery of the impurity doped HfO₂ thin film, FeFET has been considered to be the most promising non-volatile memory because of its excellent scalability and compatibility with the CMOS fabrication process.

In the case of FTJ memory, Esaki proposed an idea of FTJ memory in 1971 (Esaki *et al.*, 1971). Since a report of room temperature operation of FTJ (Pt/PbZr_{0.52}Ti_{0.48}O₃ or BaTiO₃/SrRuO₃) in 2002 (Contreras *et al.*, 2002), many investigations aiming at a high On-Off ratio and low power consumption have been reported.

Basic Properties of Ferroelectric Material

Ferroelectricity

We briefly explain the fundamental properties of ferroelectricity (Ishibashi, 2020; Kong *et al.*, 2018; Hwang and Mikolajick, 2019; Bain and Chand, 2017). Ferroelectric material has a spontaneous polarization (P_s), which can be reversed by applying an external electric field. When we apply an electric field to a FC, which usually consists of a ferroelectric thin film sandwiched by two electrically conducting plates between them, we obtain a polarization-electric field (P-E) hysteresis curve as shown in Fig. 1. An electric displacement (D) of dielectric materials including ferroelectric material is

$$D = P + \epsilon E, \quad (1)$$

where ϵ is permittivity and E is electric field in the ferroelectric material. Since polarization is usually much larger than ϵE for most ferroelectric materials, the vertical axis as shown in the Fig. 1 is often designated by P instead of D . Firstly, we define fundamental terms using for FM according to the P-E curve. A coercive field (E_c) is defined as the strength of the electric field at which the macroscopic polarization of the FC disappears, where superscripts $\pm$ are used when explaining each E_c in the positive and negative electric field direction in distinction from each other. Polarization remaining in the absence of an electric field is called the remnant polarization P_r , where superscript $\pm$ are used when explaining each P_r in the positive and negative polarization direction in distinction from each other. In a FM, stored data are read by measuring the voltage derived by polarization reversal or non-reversal current. " $2P_r$ " we refer later means the sum of absolute values of P_r^+ and P_r^- . In inner part of a dielectric material, the relation between a dipole moment (μ) and an internal electric field (E_{in}) induced by an external electric field is described following;

$$\mu = \alpha_p E_{in}, \quad (2)$$

where α_p is a polarization coefficient. Polarization in a unit cell (P) is described by

$$P = N\mu = N\alpha_p E_{in},$$

where N is the number of atoms per unit volume. And E_{in} is described as

$$E_{in} = E + \beta_L P, \quad (3)$$

where β_L is the Lorentz factor, which is described for the cubic crystal symmetry system as

$$\beta_L = \frac{1}{3\epsilon_0}, \quad (4)$$

where ϵ_0 is the vacuum permittivity. Electric susceptibility (χ) is expressed by;

$$\chi = \frac{N\alpha_p}{\epsilon_0(1 - N\beta_L\alpha_p)} \quad (5)$$

Therefore, we obtain a permittivity of the ferroelectric film (ϵ_f) as

$$\epsilon_f = 1 + \chi = 1 + \frac{N\alpha_p}{\epsilon_0(1 - N\beta_L\alpha_p)} \quad (6)$$

Since N relates to the material density and usually depends on temperature (T), $N\beta_L$ varies with temperature. When the value of $N\beta_L\alpha_p$ goes to 1, ϵ_f should diverge to infinity, which means a phase transition occurs at the critical temperature corresponding to $N\beta_L\alpha_p = 1$. When we heat a ferroelectric material, we can observe that the ferroelectric material with a low crystalline symmetry transforms to a paraelectric material with a high crystalline symmetry at phase transition temperature T_0 . In addition, "Clasius-Mossotti's relation is obtained from Eqs. (4) and (5), as the following equation for cubic crystalline system.

$$\frac{N\alpha_p}{3\epsilon_0} = \frac{\epsilon - 1}{\epsilon + 2}. \quad (7)$$

Free energy

Free energy of ferroelectric material (f) is usually described by the Landau free energy function using polarization component as an order parameter. We consider simple ferroelectric system and simply describe the Landau free energy by taking sixth order of polarization without strain energy (Devonshire, 1954; Landau, 1937).

$$f = f_0(T) + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 - EP. \quad (8)$$

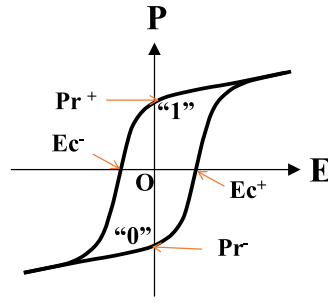


Fig. 1 Schematic P-E hysteresis curve.

Although $f_0(T)$ is a factor independent of polarization and strain, we ignore it for simplicity in this text. Odd power terms don't appear because the free energy does not depend on the polarization direction. α can be expanded as $a(T - T_0)$ around the phase transition temperature T_0 , called Curie-Weiss temperature, as;

$$\alpha = a(T - T_0) \quad (9),$$

where a is a positive number whose inverse is called "Curie constant." In the equilibrium state in the absence of an external electric field, the partial differential of the free energy (8) concerning P should be zero;

$$\frac{\partial f}{\partial P} = \alpha P + \beta P^3 + \gamma P^5 - E = 0 \quad (10)$$

Then, we obtain the following relation;

$$E = \alpha P + \beta P^3 + \gamma P^5 \quad (11)$$

Substituting P for P_0 in Eq. (11), χ in the equilibrium state is obtained by partially differentiating Eq. (10) concerning p ;

$$\chi = \frac{1}{\frac{dE}{dP}} = \frac{1}{a(T - T_0) + 3\beta P_0^2 + 5\gamma P_0^4} \quad (T < T_0) \quad (12)$$

$$\chi = \frac{1}{a(T - T_0)} \quad (T > T_0) \quad (13)$$

Phase transition

When the sign of the factor β of the fourth power term in P in Eq. (8) is positive, a phase transition from a paraelectric phase to a ferroelectric phase is continuous, which is called the second-order phase transition. In the equilibrium state, the sixth power term in P can be neglected because it is much smaller than other terms. Thus, from Eq. (10) with $E = 0$ and $\gamma = 0$, we can obtain spontaneous polarization P_s as P_0 in this situation,

$$P_s = \pm \sqrt{-\frac{\alpha}{\beta}}, \quad (14)$$

when temperature is below the transition temperature ($T < T_0$) or $\alpha < 0$, while

$$P_s = 0, \quad (15)$$

when temperatures are equal or above the transition temperature T_0 ($T \geq T_0$) or $\alpha > 0$.

The ferroelectric phase transforms to the paraelectric phase at $T = T_0$ in case of the second order phase transition. Since P_s of the ferroelectric phase decreases with increasing temperature, compensating charge emerges on the surface, which is so called pyroelectric effect. In the second order transition, electric susceptibility of Eq. (11) is expressed as;

$$\chi = -\frac{1}{2a(T - T_0)} \quad (T < T_0) \quad (16)$$

Relations between f and p , between P_s and T , between χ and T are shown in Fig. 2 (a)-(c), respectively. It should be noted that as P_s decreases with temperature increasing, the FM's retention ability generally decreases with increasing temperature.

When β in Eq. (8) is negative, phase transition from paraelectric phase to ferroelectric phase is discontinuous, which is called the first-order phase transition. Most ferroelectric materials belong to this category. In the equilibrium state without external field E , Eq. (11) should be zero. The free energy of the ferroelectric phase is equal to that of paraelectric phase at T_0 . In this text, free energy of the paraelectric phase is zero because of ignoring f_0 in the Eq. (8), thus Eq. (8) should be zero at T_0 . We obtain following equations,

$$\frac{\alpha}{2} + \frac{\beta}{4} P^2 + \frac{\gamma}{6} P^4 = 0 \quad (17),$$

$$\alpha + \beta P^2 + \gamma P^4 = 0 \quad (18)$$

In this equilibrium state of the first-order phase transition near T_0 , we rewrite the phase transition temperature T , its corresponding α , and polarization P as T_c , α_c and P_c , respectively. T_c is called Curie Temperature.

From Eqs. (17) and (18), we obtain following equations;

$$\alpha_c = \frac{3\beta^2}{16\gamma} \quad (19)$$

$$P_c^2 = \frac{-3\beta}{4\gamma} \quad (20)$$

And from Eq. (19), we obtain the T_c as;

$$T_c = T_0 + \frac{\alpha_c}{a} \quad (21)$$

In the first-order phase transition, spontaneous polarization holds even from T_0 to $T_0 + \frac{\alpha_c}{a}$. From Eq. (18), spontaneous polarization P_s^2 below T_c can be obtained as;

$$P_s^2 = \frac{2}{3} P_c^2 \left(1 + \sqrt{1 - \frac{3\alpha}{4\alpha_c}} \right) \quad (22)$$

Electric susceptibility below T_c can be obtained by differentiating Eq. (10) concerning P ;

$$\chi = \frac{1}{\alpha + 3\beta P_c^2 + 5\gamma P_c^4} = \frac{1}{\frac{16\alpha_c}{3} \sqrt{1 - \frac{3\alpha}{4\alpha_c}} \left(1 + \sqrt{1 - \frac{3\alpha}{4\alpha_c}} \right)} \quad (T < T_c) \quad (23)$$

$$\chi = \frac{1}{\alpha} \quad (T > T_c) \quad (24)$$

Polarization dependence of the free energy, temperature dependence of P_s and χ in case of the first order phase transition are shown in Fig. 3 (a)-(c). It should be noted that χ obtained by approaching T_c from ferroelectric phase is;

$$\chi^- = \frac{1}{4\alpha_c} \quad (25)$$

and that obtained by T approaching from paraelectric phase to T_c (χ^+) is;

$$\chi^+ = \frac{1}{\alpha_c} \quad (26)$$

Thus, χ has a different value at T_c by four times, depending on whether T_c approaching from ferroelectric phase or from paraelectric phase to T_c .

P-E hysteresis curve

We describe the relation between polarization and external electric field for the second-order phase transition without external force in a ferroelectric phase. From Eq. (11) with ignoring the term of γP^5 , the P-E hysteresis curve is depicted in Fig. 4. When a ferroelectric phase having $-P_s$, corresponding to the point A ($E = 0$), as shown in Fig. 4, is applied by a positive electric field E , its polarization state goes toward the inflection point B with increasing E . Although Eq. (11) shows a continuous curve from the inflection point B to the point B', as shown by dashed curve, this trajectory is never observed. Thus, polarization state of the ferroelectric phase should jump to the point C from the point B, as shown by solid curve. Then, when decreasing E , the polarization state goes to the point B' through the point A' ($E = 0$) and jumps to the point C'. A typical P-E curve, as we usually

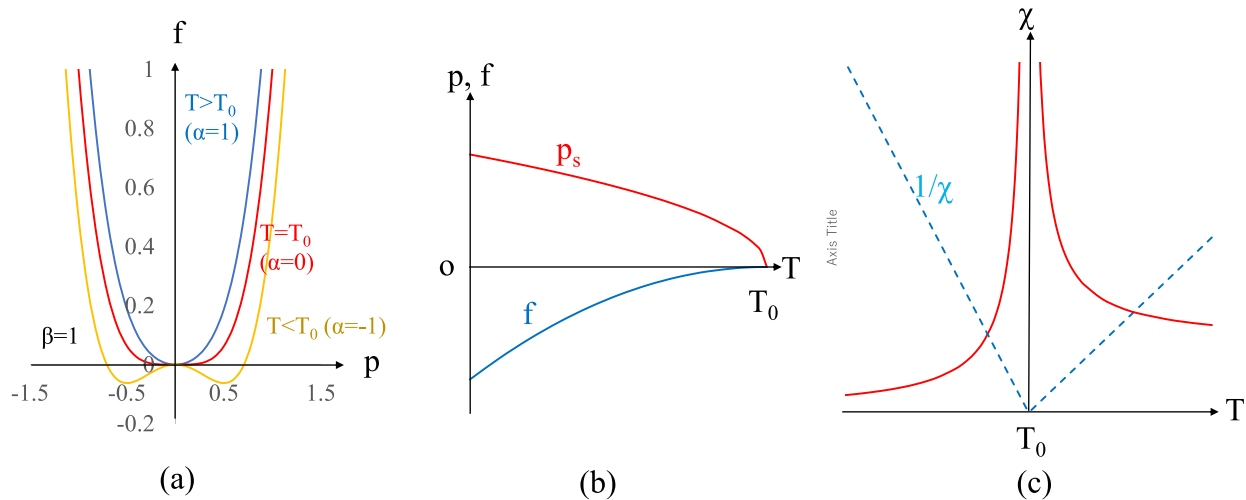


Fig. 2 Polarization dependence of Free energy (a), temperature dependence of P_s (b) and χ (c) in the case of second order phase transition.

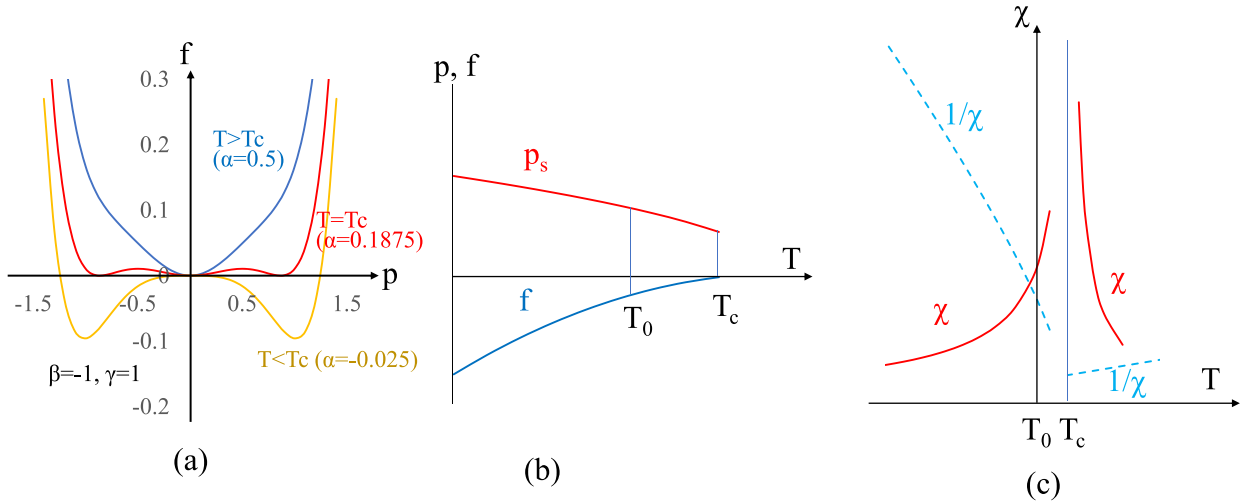


Fig. 3 Polarization dependence of Free energy (a), temperature dependence of P_s (b) and χ (c) in the case of first order phase transition.

obtain in our experiments, is like the shape depicted in Fig. 1 rather than that shown in Fig. 3 due to reflecting experimental conditions such as circuit delay so on. From the total derivative of Eq. (11) concerning P as;

$$\frac{dE}{dP} = \frac{1}{(\alpha + 3\beta P^2)} \quad (27)$$

When $(\alpha + 3\beta P^2)$ goes to zero, $\frac{dE}{dP}$ diverges to infinity. This situation corresponds to the points that polarization jumps from the point B to C and from the points B' to C'. Thus, we can obtain $\pm E_c$ from the relation;

$$\alpha + 3\beta P^2 = 0 \quad (28)$$

We obtain E_c as;

$$\pm E_c = \pm \sqrt{\frac{-4\alpha}{27\beta}}, \quad (29)$$

where double sign is in same order. As Eq. (29), the absolute value of E_c decreases with temperature approaching to T_0 , which is one of the important properties of ferroelectric memories used in FM because polarization reversal is getting to easily occur with temperatures approaching to T_0 , memory retention is getting worse.

Crystalline Symmetry

Anisotropic properties of materials, such as ferroelectricity and piezoelectricity, depend on their crystalline symmetry. When increasing temperature of a ferroelectric material, ferroelectric phase with a low crystalline symmetry generally transforms to paraelectric phase with a high crystalline symmetry. For example, while crystalline structure of lead titanate (PbTiO_3 or PTO), a typical ferroelectric material, belonging to a perovskite family as shown in Fig. 5, has a tetragonal crystalline symmetry where the c axis is slightly longer than the two other axes resulting in appearance of p_s along the c axis below T_0 , it has a cubic crystalline symmetry where each length of the crystalline axes a , b , and c is equal above T_0 . The Ti^{4+} ion occupies one of the two stable positions, which exist slightly upper and lower position from the center of a unit cell.

Ferroelectric Materials and Ferroelectric Memory

Ferroelectric Materials

After Valasek discovered the ferroelectricity for the first time in 1920 (Valasek, 1920) in Rochelle salt, various ferroelectric materials have been discovered. In this section, we briefly introduce typical ferroelectric materials used in FM.

Perovskite ferroelectric materials

Perovskite ferroelectric materials are commonly used for FM. The first man-made ferroelectric material is barium titanate (BaTiO_3), which is invented as a piezoelectric material for submarine sonar during World War II. BaTiO_3 or its solid solution with SrTiO_3 often used as piezoelectric transducers, dielectric amplifier so on taking their advantages of high piezoelectric constants and dielectric constant. However, BaTiO_3 and its related materials are not necessarily used as ferroelectric materials for FM maybe due to low T_c under 120°C (von Hippel, 1950). Lead zirconate (PbZrO_3 or PZO), lead titanate (PbTiO_3 or PTO) and their solid

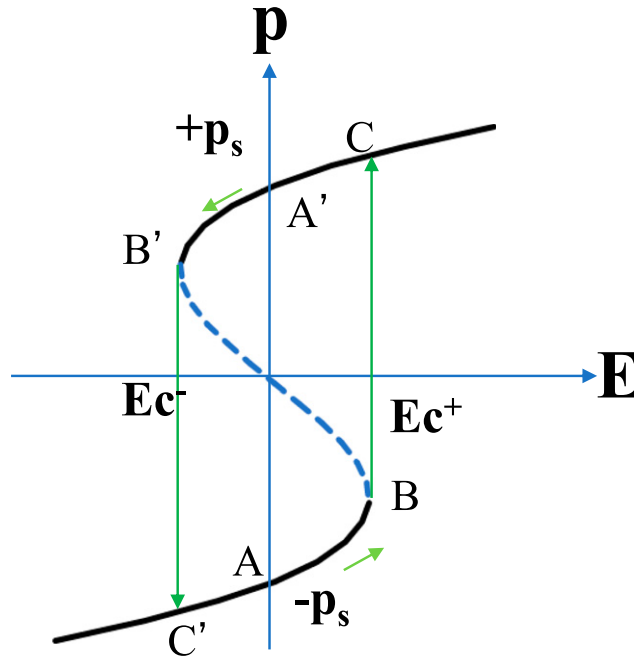


Fig. 4 A theoretical P-E hysteresis curve derived from Eq. (10) in the case of second phase transition.

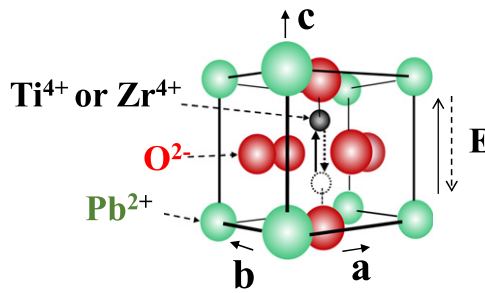


Fig. 5 A schematic atomic structure of PZT.

solution system ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ($0 < x < 1$) or PZT), belonging to the perovskite family, are the most important ferroelectric materials being used by most commercialized FMs. T_c of PTO is reportedly about 490°C (Jaffe *et al.*, 1955). Although Shirane *et al.* reported that Waku and Hori found the phase transition of PTO in 1949 (Shirane and Hoshino, 1951), Shirane *et al.* substantially found the ferroelectricity of PTO and PZT at first time, (Shirane and Takeda, 1952). In the PZT system, Zr/Ti atomic ratio affects its crystalline structure and T_c . Jaffe *et al.* investigated phase diagram of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ as shown in Fig. 6 (Jaffe *et al.*, 1971). While $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ has a cubic crystal system (Cubic phase or F_c) that is paraelectric at high temperatures, it has a tetragonal crystal system (Tetragonal phase or F_T , $x > 0.52$) and a rhombohedral one (Rhombohedral phase or F_R , $x < 0.52$) that are all ferroelectrics at low temperatures. The “ R_T ” phase actually had been found consisting of two parts by the measurement of electrical properties and thermal expansion and also by neutron measurement (Michel *et al.*, 1969). The P_s in the “ F_T ” phase is along $< 100 >$ direction and that in the “ F_R ” phase is along $< 111 >$ direction. In the phase diagram, the tetragonal-rhombohedral boundary (composition ratio is nearly $x = 0.52$) is called the morphotropic phase boundary (MPB). Impurity doped PZT is usually used for capacitors in FMs, as it has been reported that doping with La (Sudhama *et al.*, 1993; Zhu *et al.*, 1996) or Nb (Chai *et al.*, 1995; Boyer *et al.*, 1997) is effective for improving the leakage current, fatigue and imprint of PZT capacitors. Fox *et al.* reported that La and alkaline earth metals doping can reduce the saturation voltage of PZT, which lowers the operation voltage of the FRAM (Fox *et al.*, 2001). In the late 1980s and early 1990s, many attempts were made to apply PZT to DRAM capacitors to increase their capacitance, and so increase memory density (Carrano *et al.*, 1989; Torii *et al.*, 1995).

Since the beginning of the 21st century, BiFeO_3 (BFO), which also belongs to a perovskite family, has attracted much attention because it is an antiferromagnetic, ferroelectric multiferroic with T_c of about 820°C and a Neel temperature of about 370°C . In particular for magnetoelectric devices such as MRAM, it is much advantageous to control its ferromagnetism by electric field (Chu *et al.*, 2008). Although BFO has a larger $2P_r$ ($\sim 100 \mu\text{C}/\text{cm}^2$) and a low deposition temperature (Wang *et al.*, 2003), it has a large coercive field ($\sim 550 \text{ kV}/\text{cm}$ – the E_c of PZT is $\sim 65 \text{ kV}/\text{cm}$) and large leakage current which has limited its application not only to

FM but also other electric devices. Doping with impurities has reportedly proved to be effective in improving electric properties (Hu *et al.*, 2008). (Kawae *et al.*, 2009; Mao *et al.*, 2016).

Other important perovskite family are Bi-layered perovskite materials (also referred to as "Aurivillius phase") (Aurivillius, 1949; Smolenskii *et al.*, 1959a) whose crystal structure consists of a $(\text{Bi}_2\text{O}_7)^{2+}$ sub-layer and a $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ ($n \geq 2$, integers) perovskite sub-layer, where A and B stand for cations (Smolenskii *et al.*, 1959b,c). This type of perovskite has various structures depending on the combination of these sub-layers. A schematic crystalline structure of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT), a typical Bi layered perovskite, is shown in Fig. 7 (Liu *et al.*, 2003). In 1974, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), a layered perovskite family, was applied to Si-based FM by Wu (1974). In 1995, Araujo *et al.* found that SBT, $\text{SrBi}_2\text{NbTaO}_9$ (SBTN) and $\text{SrBi}_4\text{Ta}_4\text{O}_{15}$ have an immune to fatigue (see Section "Classification of FRAM Degradation and Reliability Assessment"), which is attributed to their structural flexibility (de Araujo *et al.*, 1995) and FRAM using SBT or SBTN has been developed by many companies (Fujii *et al.*, 1997; Eshita *et al.*, 1999; Park *et al.*, 1999). Both SBT and SBTN have smaller coercive fields and saturation polarizations than PZT.

HfO₂ based ferroelectric material

HfO₂-based or fluorite-based ferroelectric material ($\text{HfO}_2\text{-Fe}$), including impurity doped HfO_2 and $\text{HfO}_2\text{-ZrO}_2$ solid solution (HZO), have attracted much attention with an expectation to realize an unprecedented NVM having a high density and a high speed since Börscke *et al.* discovered the ferroelectricity of Si doped HfO_2 for the first time in 2011 (Boescke, 2008 (filling); Börscke *et al.*, 2011; Müller *et al.*, 2011a) because HfO_2 , a well-known high-k gate insulator material, has good compatibility of CMOS fabrication process. And it also has been reported that $\text{HfO}_2\text{-Fe}$ has good electric properties, such as large $2P_r$ above $10 \mu\text{C}/\text{cm}^2$, low leakage current even with its thickness of 10 nm or less. However, E_c of $\text{HfO}_2\text{-Fe}$ is about 1 MV/cm which is 10 times higher than that of PZT. Fortunately, we can apply a thin $\text{HfO}_2\text{-Fe}$ film to FM by taking advantages of low leakage current (Boescke, 2008 (filling)), which can work even at a low voltage.

In the crystallographic view point, HfO_2 has a monoclinic phase (m-phase) with a space group of $P2_1/c$ around the room temperature, which martensitically transforms to a tetragonal phase (t-phase) with a space group of $P4_2/nmc$ over 1700°C and further transforms to a cubic phase (c-phase) with a space group of $Fm\bar{3}m$ over 2600°C under the atmospheric conditions (Wang *et al.*, 1992; Shin *et al.*, 2006). Since those crystalline structures are all centrosymmetric, most researchers did not consider HfO_2 exhibiting ferroelectricity. It has been found that ferroelectricity of HfO_2 was originated from the formation of an orthorhombic phase (o-phase) with a space group of $Pca2_1$ or the rhombohedral phase with the space group $R\bar{3}$ (Börscke *et al.*, 2011; Wei *et al.*, 2018). However, the o-phase only appears at a high pressure over 4 GPa according to the bulk phase diagram of HfO_2 (Ohtaka *et al.*, 1991). Why does the o-phase appear under certain conditions? Xu *et al.* found that almost the same value of $2P_r$ appeared irrespective of dopant species, as shown in Fig. 8 (Toriumi *et al.*, 2019), so that they conclude the ferroelectricity is intrinsic property of HfO_2 (Xu *et al.*, 2017). It has been considered that ferroelectric o-phase should be stabilized by doped impurity or ZrO_2 co-solution. However, the free energy difference between the ferroelectric o-phase and the stable m-phase is too large to be overcome by doping alone (Batra *et al.*, 2017). Thus, various mechanisms such as oxygen vacancy, surface energy effect, have been proposed to describe the unexpected formation of the metastable o-phase (Park and Schroeder, 2019; Mikolajick *et al.*, 2021). In the application of $\text{HfO}_2\text{-Fe}$ to FM, a

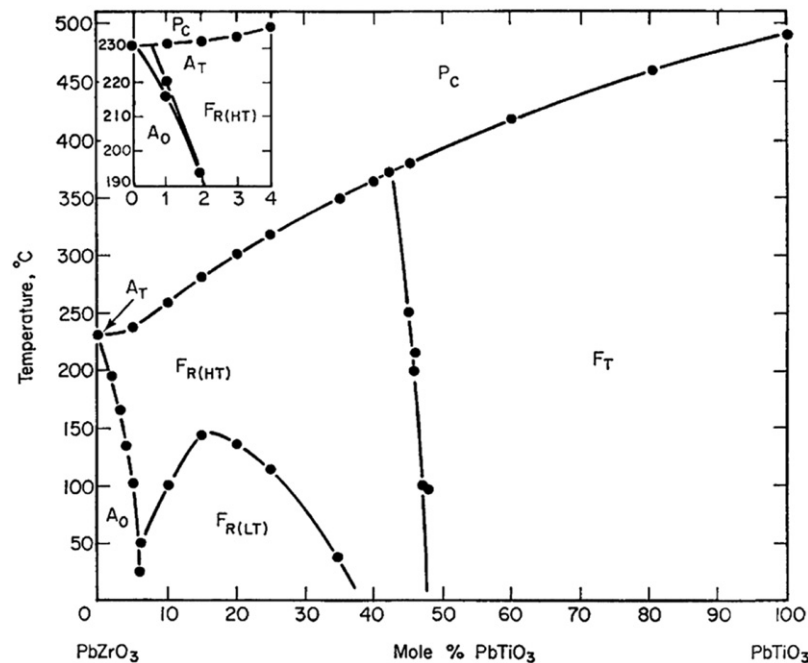


Fig. 6 A phase diagram of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (Jaffe, 1971).

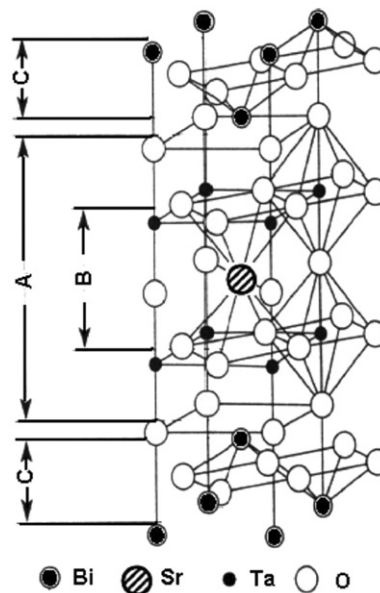


Fig. 7 A schematic crystalline structure of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT). Reproduced from Liu, H., Min, X., Sun, X., Xiao, J., Ouyang, S., 2003. Structural and electronic properties of SBT in FEDREAM devices. *Solid-State Electronics* 47, 2283–2287. Available at: [https://doi.org/10.1016/S0038-1101\(03\)00213-2](https://doi.org/10.1016/S0038-1101(03)00213-2).

number of demonstration have been reported such as capacitor type FRAM (Müller *et al.*, 2013; Polakowski *et al.*, 2014), FeFET (Boescke, 2008 (filling); Alia *et al.*, 2018), FTJ memory (Chernikova *et al.*, 2016; Tian *et al.*, 2016; Fujii *et al.*, 2020).

Other ferroelectric materials and antiferroelectric materials

Fichtner *et al.* demonstrated ferroelectric switching of a III-V semiconductor-based material of $\text{Al}_{1-x}\text{Sc}_x\text{N}$ ($x \geq 0.28$) in 2019 (Fichtner *et al.*, 2019). Advantages of the $\text{Al}_{1-x}\text{Sc}_x\text{N}$ ferroelectric film for application CMOS based memory are its high $2P_r$ of about $100 \mu\text{C}/\text{cm}^2$ and low deposition temperature of 400°C . However, there are some disadvantages of $\text{Al}_{1-x}\text{Sc}_x\text{N}$, such as relatively high leakage current and a large E_c of $3 \text{ MV}/\text{cm}$. Kataoka *et al.* (2021) reported that the origin of leakage current and it was caused by formation of nitrogen vacancies.

Since the strong piezoelectricity of polyvinylidene difluoride (PVDF) was discovered in 1969 (Kawai, 1969) and its ferroelectricity was suggested in 1971 (Bergman *et al.*, 1971), many proposals of its application to NVM have been reported (Ng *et al.*, 2012; Khan *et al.*, 2012; Khikhlovskiy *et al.*, 2013; Ghittorelli *et al.*, 2017; Li *et al.*, 2019b). All organic NVM consisting of organic ferroelectrics and organic transistors have been expected to realize a transparent, flexible and wearable FM with a low production cost (Chen *et al.*, 2017). Jang *et al.* (2019) proposed artificial synapses that features freestanding ferroelectric organic neuromorphic transistors. Most organic FM's have FeFET structure, as described in the section "FeFET". Although organic FM have not commercialized yet, it is a promising technology to be applicable not only to industrial devices but also to electric devices commonly used for our everyday life.

It should be worth noting antiferroelectric materials applying to NVM. Antiferroelectrics have not been considered as NVM elements because a removal of the external field causes a depolarization, resulting in a loss of the stored information, as schematic P-E hysteresis shown in Fig. 9. However, various proposals of antiferroelectric application to NVM have been reported because of their good fatigue endurance (Pešić *et al.*, 2016; Liu *et al.*, 2018; Ali *et al.*, 2019). Pešić *et al.* proposed to apply ZrO_2 , an antiferroelectric material, to NVM using electrodes with different workfunction to induce an internal bias field (Pešić *et al.*, 2016), which shifts the P-E hysteresis curve resulting in storing information.

Capacitor Type FRAM

Structure and production method

Commercialized Si-based FRAMs are usually fabricated by combining production of FCs and complementary metal–oxide–semiconductor (CMOS). Since the deposition and/or crystallization temperature(s) of ferroelectric material such as PZT and SBT, typically $700\text{--}800^\circ\text{C}$ (Yamazaki *et al.*, 1997; Noguchi *et al.*, 1996), needs higher than those of the metallization process, fabrication process of FC is usually inserted between a transistor fabrication process (front end of line: FEOL) and a metallization process (back end of line: BEOL) (Fujii *et al.*, 1997; Yamazaki *et al.*, 1997; Moise *et al.*, 1999; Horii *et al.*, 2002). In comparison with the FLASH memory process, where an additional high voltage transistor fabrication process is needed, the FRAM process is much simpler, because FRAM memory cells can use logic transistors "as is". This is especially advantageous when fabricating FRAM embedded logic devices. Noble metals, such as Pt, Ir and IrO_2 , are usually employed for capacitor electrodes for the same reason (and also because they have high work functions).

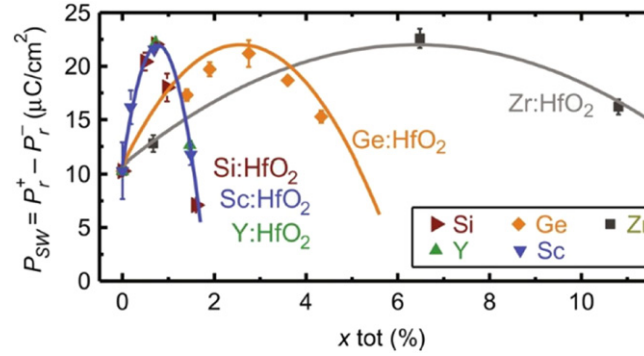


Fig. 8 Switchable polarization ($P_r^+ - P_r^-$) of HfO_2 films as a function of the doping concentrations, $x\%$ for different dopants: Sc, Y, Si, Ge, Zr, and N, where switchable polarization is defined by $P_r^+ - P_r^-$ in this reference Toriumi *et al.* Reproduced from Toriumi, A., Xu, L., Shibayama, S., Migita, S., 2019. Ferroelectric films by physical vapor deposition and ion implantation. In: Schroeder, U., Hwang, S., Funakubo, H. (Eds.), *Ferroelectricity in Doped Hafnium Oxide*. pp. 110 125, Woodhead Publishing.

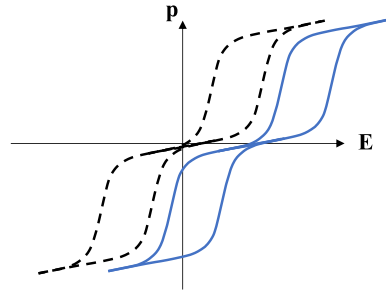


Fig. 9 A schematic P-E hysteresis curve of antiferroelectric material. solid blue and Dashed black curves are P-E hysteresis with and without induced internal electric field, respectively.

There are two different types of FC configuration (Eshita *et al.*, 2014). One is planar capacitor structure (Fujii *et al.*, 1997; Yamazaki *et al.*, 1997), and the other is a stacked capacitor structure, (Moise *et al.*, 1999; Horii *et al.*, 2002). Schematic structures are depicted in Fig. 10 (a) and (b). Although planar capacitor type is relatively more easily fabricated than stacked type, it costs cell area. Thus, recent most high density FRAM structure has stacked capacitor type.

In the fabrication process of the planar capacitor, a FC is placed above field insulator layers (generally referred to as shallow trench isolation (STI) or local oxidation of silicon (LOCOS) after planarization of a dielectric layer over the metal oxide semiconductor field-effect transistor (MOSFET). Electrical contacts between the capacitor electrodes and the MOSFETs are made following dielectric interlayer deposition over the capacitor. This process is relatively easier than the stacked capacitor process, though the unit memory cell area is larger.

In the stacked capacitor process, a bottom electrode of FC is disposed directly onto the contact metal (usually W) connecting to a MOSFET, a very fine bottom electrode structure, and/or materials have to be employed to avoid the oxidation of the contact metal during the high temperature ferroelectric process. Oxygen barrier metal such as TiN, TiAlN, Ir, IrO_2 and/or their stacks are commonly used for a bottom electrode (Hugon *et al.*, 1999; Sakoda *et al.*, 2001). The stacked capacitor has the advantage of small memory cell area, even though the fabrication process and materials required are slightly more complicated than those of a conventional planar CMOS process. For ferroelectric film formation, physical vapor deposition (PVD) mainly using sputter deposition (Ishida *et al.*, 1977; Yamazaki *et al.*, 1997), metal organic chemical vapor deposition (MOCVD) (Van Buskirk *et al.*, 1998; Moise *et al.*, 1999; Horii *et al.*, 2002) or chemical solution deposition (CSD) mainly using spin coating (Budd *et al.*, 1986; Boyle *et al.*, 1996), have been employed. Electrodes are usually deposited by PVD. Although the deposition costs of PVD and CSD are relatively lower than MOCVD due to low source cost and high throughput, the MOCVD method has the advantage of precise source material controllability.

One of the important points in the FRAM fabrication process is that oxide ferroelectric materials are easily reduced by hydrogen or hydroxyl, which is generated from H_2O or organic materials. It results in crucial degradation or disfunction of FC (Aggarwal *et al.*, 1998; Cross *et al.*, 2001). Thus, the capacitor type FRAM generally employs “hydrogen barrier” layer encapsulating FCs to eliminate the ferroelectric degradation from hydrogen (Park *et al.*, 1997; Sakoda *et al.*, 2001; Nagano *et al.*, 2005; Chowdhury *et al.*, 2007). Other important points are optimization of the crystalline quality of ferroelectric film and electrode, atomic interdiffusion between ferroelectric film and electrode (Nomura *et al.*, 2018; Wang *et al.*, 2019; Nomura *et al.*, 2020). Nomura *et al.* (2020) reported that optimization atomic interface diffusion was effective to lower the E_c resulting in lowering operation voltage with keeping a high value of $2P_r$. While most stacked capacitor type FRAM have a capacitor-under-bitline (CUB) structure, Saito *et al.* successfully demonstrated a capacitor-over-bitline (COB) structure, which has been usually employed by DRAM, to lower the memory cell area (Saito *et al.*,

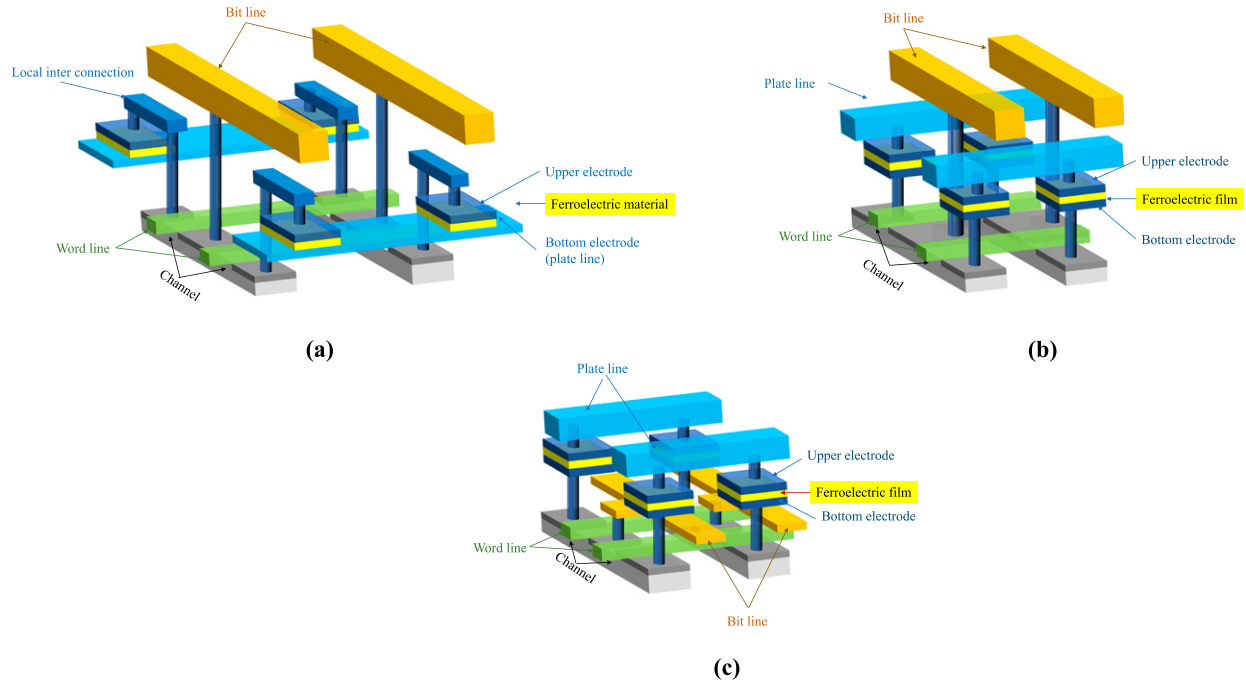


Fig. 10 Schematic structure of capacitor type FRAM varieties. A planar type (a), A stacked type (b), and a stacked type with capacitor over bit line (c).

2015) as shown in Fig. 10(c). To produce high density FRAM, wafer bonding technology is promising. Maeda *et al.* thinned the capacitor type FRAM fabricated wafers to 9 μm and stacked them by their wafer-to-wafer bonding technology. They reported electric properties including polarization, junction leakage current not changed even after wafer thinning and bonding processes (Maeda *et al.*, 2010). In the FC etching process, conventional reactive ion etching (RIE) cannot be employed since noble metals, which are used both for top and bottom electrodes, are not reactive and the vapor pressures of by-products from ferroelectric materials are extremely low. Therefore, physically-assisted RIE is employed by using argon-mixed etching gases.

$\text{HfO}_2\text{-Fe}$ has attracted many researchers because of its good compatibility with CMOS process. Although the crystallization temperature of $\text{HfO}_2\text{-Fe}$ was reportedly around 600–650°C for the first time (Müller *et al.*, 2011b), recent reports showed that $\text{HfO}_2\text{-Fe}$ capacitor was able to be integrated into BEOL by lowering $\text{HfO}_2\text{-Fe}$ crystallization temperature to 500°C or less (Okuno *et al.*, 2020; Tahara *et al.*, 2021). Polakowski *et al.* (2014) characterized three-dimensional (3D) trench capacitor fabricated using Al doped HfO_2 and obtained good electric properties. Thus TiN, a material commonly used in CMOS process, can be applied to electrode as an electrode metal for FC which results in precise capacitor patterning. Therefore, FRAM with $\text{HfO}_2\text{-Fe}$ can be produced by fully compatible CMOS production process which means FRAM with $\text{HfO}_2\text{-Fe}$ is a potential “game changer” for NVM in the near future (Müller *et al.*, 2014).

Circuit and Operation of Capacitor Type FRAM

Write/read operation in the capacitor-type FRAM with a DRAM-like memory cell

We briefly explain the basic write/read operation of a capacitor-type FRAM with a DRAM-like memory cell. Schematic circuits of the capacitor-type FRAM with a DRAM-like memory cell is shown in Fig. 11, where a unit memory circuit is shown by the blue square. In a write operation, first the bit line is set to a high or low level. After turning on the selection transistor, a voltage pulse is applied to the plate line. Data “0” is written on the capacitor while line turns back to the low level. This operation allows bi-directional application of the full supply voltage to the capacitor, switching the polarization sufficiently. In a read operation, the bit line is firstly pre-charged at 0 V and then set to floating. After turning on the selection transistor and driving the plate line to the high level, charge flows to the bit line from the cell capacitor, resulting in a bit line voltage increase. While polarization reversal charges flow to the bit line when reading “1”, linear charges flow to the bit line when reading “0”. The increase in the bit line voltage from reading “1” is usually larger than that from reading “0”, because the polarization reversal charge is larger than the linear charge. A sensing amplifier connected with a bit line determines the “1” or “0” by comparing a “reference voltage” generated by the designated FC or a setting voltage. Note that the above-mentioned read operation for FRAM is sometimes called “a destructive read”, because it needs polarization reversal to read data. The polarization reversal charge depends on condition of the FC, which could become small if the capacitor is degraded by depolarization, imprint or fatigue as mentioned below. This reading operation is called a “High-Z” sensing scheme, which means a high impedance. In this scheme, externally supplied voltage (V_{dd}) is not fully applied to each cell capacitor, because the supplied voltage is reduced by $\frac{C_b}{C_b+C_f}$ due to the floating bit line, where C_f and C_b are the capacitance of FCs and bit line, respectively. To improve the sensing margin in high

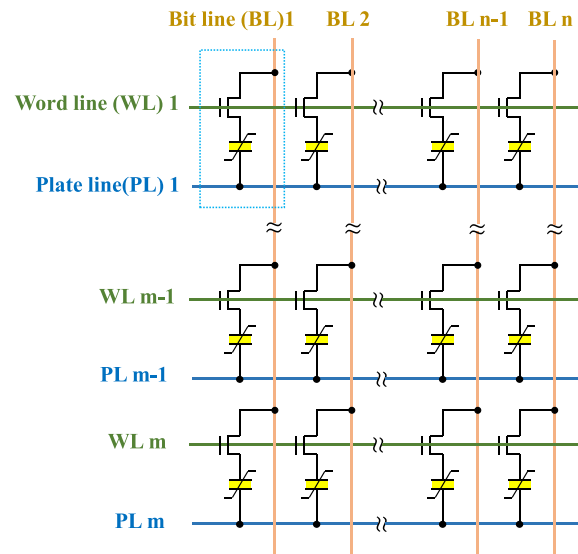


Fig. 11 Schematic circuit diagram of capacitor type FRAM's memory array.

density FRAMs, a “bit line ground sensing” (BGS) technique has been proposed by Kawashima *et al.* (2002). In their sensing scheme, since the p-MOS charge transfer maintains the bit line level near to ground when the plate line is high, almost the entire external voltage can apply to each cell capacitor, which results in a drastic increase in the sensing margin.

There are some methods to enhance the reliability of FM. Two-transistor and two-capacitor (2T2C) type FRAM strengthen memory retention by pairing two memory units. Two FCs in the paired units are polarized by opposite direction each other, the sensing amplifier determine the “0” or “1” by cross referencing the paired memory units. It should be noted that FRAM using one memory unit is called one-transistor and one-capacitor (1T1C) type. The error correcting code (ECC) method is employed for high reliability memories, which can check the error and correct the information by using additional memory units (parity bit) (Katayama *et al.*, 1999). For example, 64-bit memory units works with additional 8-bit parity units, thus its memory area is not larger than that of 2T2C. Application of redundant memory units is another method to correct the malfunctioned memory units. Min *et al.* (2005) proposed to use this method for one time programming scheme aiming for use in smart card, where malfunctioned memory units are replaced with previously prepared memory units by electric switching. Since FRAM with 2T2C cell structure, ECC or redundant memories needs additional memory cells which results in larger die size and longer testing time, we should determine the memory structure and circuits with respect to the balancing of robustness of the memory retention and production costs.

Capacitor-type FRAM with a SRAM-like memory cell

After Dimmer and Eaton's invention of non-volatile SRAM (Dimmler and Eaton, 1987 (filling)), many proposals of non-volatile SRAM using FC have been reported (Burnsa *et al.*, 1995; Miwa *et al.*, 2001; Masui *et al.*, 2003; Li *et al.*, 2017; Kobayashi *et al.*, 2018b; Takeuchi *et al.*, 2019). A typical memory circuit is shown in Fig. 12. Miwa *et al.* proposed non-volatile SRAM or “shadow SRAM” consisting of six transistors and two FCs for use of “application specific integrated circuit” (ASIC) (Miwa *et al.*, 2001). Takeuchi *et al.* (2019) reported the feasibility of the shadow SRAM and found that stable dynamic recall operations can be achieved by using small FCs, and that non-volatile write energy of well below 10 fJ/bit can be expected, adding minimal area penalty and performance degradation to the base SRAM cell. Masui *et al.* (2003) proposed a non-volatile SRAM with a SRAM memory cell and four FCs to improve the recall operation. They have proposed that their non-volatile SRAM, with an access speed of 4 ns, could be applied to a dynamically programmable gate array (DPGA) with high performance.

Other capacitor type FRAMs

Takashima *et al.* proposed their “chain FRAM” to realize FRAM with a large memory density by reducing memory cell area. The chain FRAM comprises parallel connection of one transistor and one ferroelectric capacitor. One memory cell block consists of multiple memory cells connected in series with a block selecting transistor. It has been reported that a unit cell area of $4F^2$ could be realized by using chain FRAM configuration (Takashima and Kunishima, 1998; Ogiwara *et al.*, 2015), where F means a feature size corresponding to the minimum size feasible in the fabrication process. Slesazek *et al.* proposed gain cell memory consisting of two transistors and two or more FCs (2TnC) which functions by combination of FRAM mode and FTJ mode aiming to realize compute-in memory algorithm (Slesazek *et al.*, 2019).

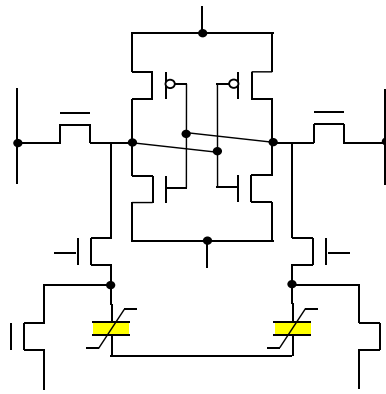


Fig. 12 Schematic circuit diagram of non-volatile SRAM's memory unit. This figure is simply redrawn from original figure Dimmler and Eaton (filling). Redrawn from Dimmler, K., Eaton Jr. S.S., 1987 (filling). Memory Cell With Volatile and Non- Volatile Portions Having Ferroelectric Capacitors. US4809225.

FeFET

As described in 2.1, there are several variations of FeFET, such as MFS, MFIS, and MFMIS. Schematic structures of these FeFET are shown in Fig. 13 (a)-(c). In the FeFET, information is stored in the gate ferroelectric layer and read out as transistor drain current, since the polarization direction of the ferroelectric layer determines the transistor threshold voltage. For example, when the polarization direction of the ferroelectric layer is downward, the threshold voltage is lower than that of polarization direction of upward as shown in Fig. 14. It is advantageous that this type of FRAM is completely scalable with transistor design, and enables non-destructive read operations. Since memory structure of the FeFET is similar to the floating gate type memories like FLASH memory, it is natural that NAND type FRAM is proposed aiming to further lower the memory area. Phillips *et al.* proposed the modeling of the MFS type FeFET NAND gate (Phillips *et al.*, 2006). Sakai *et al.* demonstrated a "Ferroelectric NAND" (Fe NAND) operating with a low program/erase voltage, 6 V and a high endurance, 10^8 cycles (Sakai *et al.*, 2008; Hatanaka *et al.*, 2009). As NAND FLASH memory has evolved to three dimensional (3D) structures, 3D FeFETs also have been proposed after the advent of HfO_2 -Fe discovery (Florent *et al.*, 2017; Van Houdt, 2017; Hsueh, 2020; Ham *et al.*, 2021). A schematic cross sectional view of 3D NAND FeFET is shown in Fig. 15. Florent *et al.* (2017) demonstrated a 3D FeFET using Al doped HfO_2 -Fe device, for NAND applications for the first time and showed an estimated time to failure more than 10 years at 85°C. Zhang *et al.* (2017) reported that a drastic data storage retention improvement as long as 10^5 s and cycling endurance of 10^9 was achieved by employing a MFIS (Pt/SBT/ HfO_2 /Si) gate structure with 3.3 V writing operation.

In the IoT era, the conventional von Neumann type computing, which has evolved with Si transistor technology trend predicted by Moore (Moore's law) (Moore, 1965), has been revealed as a major performance and energy bottleneck for rising data-intensive applications. There are almost two main strategies to beyond the Moore's law. One is in-memory computing where certain computational tasks are performed in place in the memory itself organized as a computational memory unit (Sebastian *et al.*, 2020). The effectiveness of in-memory computing heavily relies on the memory scalability, which cannot be satisfied by traditional memory technologies (Li *et al.*, 2019a). Yin *et al.* (2016) investigated FeFET for a logic-in-memory usage and concluded that their FeFET slightly out-performs a volatile CMOS equivalent in terms propagation delay and dynamic power. Reis *et al.* (2018) also chose FeFET for their in-memory computing system rather than other emerging NVM because other emerging NVMs have high writing energy, large latency and low On-Off ratio. Their proposed system has a cell structure consisting of two transistors and one FeFET, which results in low energy consumption and high-speed operation. Another strategy is neuromorphic computing which takes clues from the brain to create energy-efficient hardware for information processing (Mead, 1990; Marković *et al.*, 2020). Many researchers have made efforts to apply FeFET to the neuromorphic computing taking advantages of its electric properties, such as low energy consumption and high-speed write/read operation (Yu, 2018). In this application, the channel conductance can be changed by applying a gate voltage through a change in the ferroelectric polarization which is considered to emulate a synaptic learning function (Nishitani *et al.*, 2013; Oh *et al.*, 2019; Halter *et al.*, 2020). Mulaosmanovic *et al.* proposed a FeFET-based synapse using gradual and non-volatile ferroelectric (HfO_2 -Fe) switching with 28 nm node high-k metal gate technology (Mulaosmanovic *et al.*, 2017).

FeFET using organic ferroelectric materials is also very attractive because of its expectation for realizing flexible device. In the FeFET produced by using organic ferroelectrics, Zhao *et al.* demonstrated a unique flexible FRAM based on poly PVDF-TrFE (polyvinylene trifluoroethylene) dielectric whose memory unit consisting of one selection transistor and one FeFET (Zhao *et al.*, 2017). Khan *et al.* (2012) proposed an interesting application of organic FRAM to bank notes in which non-volatile polymer FM was printed. Li *et al.* (2019b) demonstrated organic FM with ultra-short channel length transistors resulting in obtaining a large current density and a high operating speed. Although FeFET is very promising technology, reliability such as memory retention, rewriting endurance has not been sufficiently proven. If its reliability would be proven, it would be a main memory widely used in the future devices.

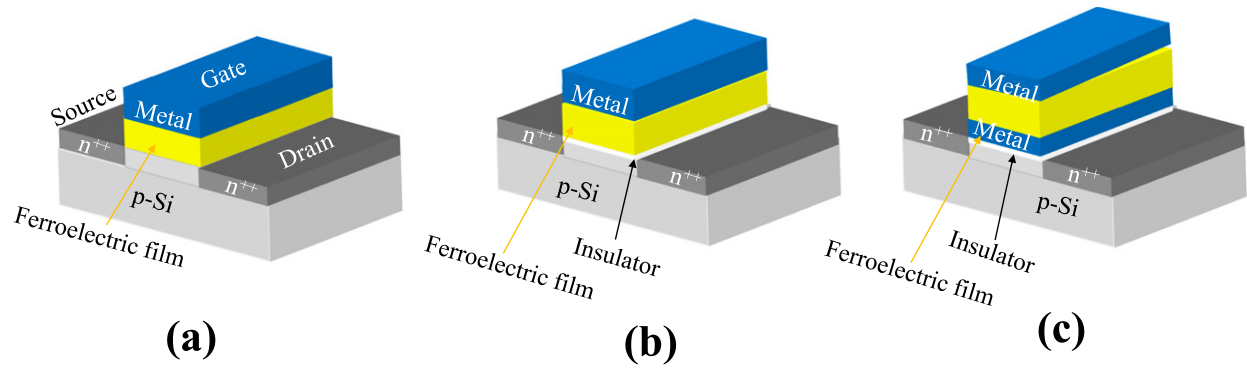


Fig. 13 Schematic drawings of tree type FeFETs. MFS gate structure(a), MFIS(b), and MFMIS structure structure(c).

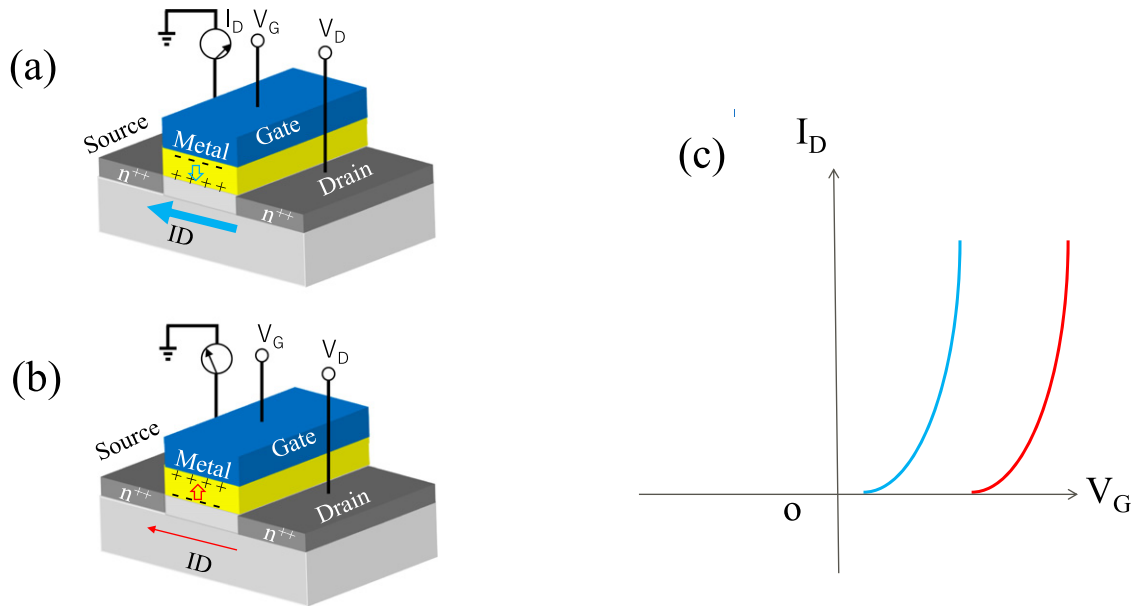


Fig. 14 A schematic explanation of FeFET function. FeFET with polarization direction of ferroelectric layer downward (a), FeFET with polarization direction of ferroelectric layer upward (b), A schematic relation between drain current vs gate voltage. Blue and red curves shows when polarization direction of ferroelectric layer downward and upward, respectively (c).

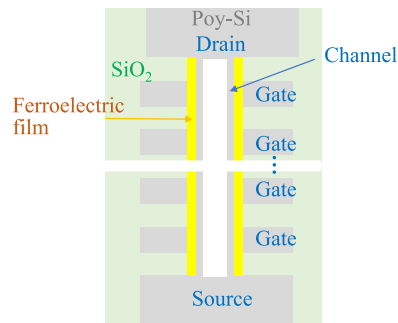


Fig. 15 A schematic cross-sectional view of the 3D FeFET. Reproduced from Florent, K., Lavizzari, S., Di Piazza, L., *et al.*, 2017. First demonstration of vertically stacked ferroelectric Al doped HfO₂ devices for NAND applications. In: Proceedings of the Symposium on VLSI Technology, Kyoto, Japan. doi:[10.23919/VLSIT.2017.7998162](https://doi.org/10.23919/VLSIT.2017.7998162).

FTJ Memory

FTJ memory is a two-terminal memory device belonging to a type of resistance change memories, which stores the information as a polarization direction of the ferroelectric film sandwiched by two electrodes and reads the stored information by sensing the tunneling current which depends on the polarization direction of the ferroelectric film. A schematic FTJ memory and its band diagram are shown in Fig. 16. It is more advantageous of FTJ memory to employ a $\text{HfO}_2\text{-Fe}$ film rather than other ferroelectrics because thickness of the $\text{HfO}_2\text{-Fe}$ films can be sub 10 nm or less, which results in large tunneling current and large On-Off ratio (Fujii *et al.*, 2016; Chernikova *et al.*, 2016).

Although the resistance of FTJ was theoretically thought to be abruptly changed by polarization switching of ferroelectric film, recent research showed that the resistance continuously changed rather than abruptly. In other word, some FTJs, depending on its fabrication process and composed materials though, behave like memristor (Chanthbouala *et al.*, 2012; Wang *et al.*, 2014) which is characterized by a continuous change in resistance with the history of current flown across the device (Chua, 1971). Thus, FTJ memristor have attracted many researchers to apply FTJ for neuromorphic devices (Ryu *et al.*, 2019; Max *et al.*, 2020). Since the mechanism of gradual change in conductance of FTJ seems to be complicated, various proposals have been reported to explain this phenomenon, for example, modulation on the barrier height model (Kohlstedt *et al.*, 2005; Zhuravlev *et al.*, 2005; Chanthbouala *et al.*, 2012; Yamada *et al.*, 2013), charge redistribution model (Kim *et al.*, 2012; Mikheev *et al.*, 2020), and both of their mixed model (Ferreya *et al.*, 2020).

Another practical challenge for FTJ is to increase On-Off ratio, many proposals have been reported, for example, one metal electrode replaced with semiconductor (Kobayashi *et al.*, 2018a). Fujii *et al.* (2016) proposed to insert a dielectric layer between ferroelectric film and electrode to limit the on-current flow (self-compliance), which is indispensable for two-terminal device. Later, high On-Off-ratio realized in this structure has been reported, (Ryu *et al.*, 2019; Max *et al.*, 2020; Boescke, 2008 (filling); Yamaguchi *et al.*, 2020).

Classification of FRAM Degradation and Reliability Assessment

Electrical degradation phenomena of FC are typically classified into three categories, “depolarization”, “imprint” and “fatigue”. These degradations are observed as an abnormality of P-E hysteresis as shown in Fig. 17. Although FeFET and FTJ have not FCs, their device degradation can be considered using these categories.

Depolarization

Depolarization is observed as $2P_r$ decreases from the original as show in Fig. 17 (a) which occurs as the ambient temperature of FRAM increased towards the T_c . Thus, the depolarization depends on time and temperature and thus one of the most persistent obstacles to realize a reliable FM. Depolarization can be enhanced when a depolarization field (E_{dep}) appears in the ferroelectric film. In case of the stacked structure of ferroelectric and dielectric films, like the gate of FeFET, Ma and Han pointed that the E_{dep} appears when the external voltage goes to zero (Ma and Han, 2002). Their derived E_{dep} using the model of ferroelectric and dielectric capacitors connected in series is following;

$$E_{dep} = \frac{p}{\epsilon_f} \frac{1}{\left(\frac{C_d}{C_f} + 1\right)} \quad (29)$$

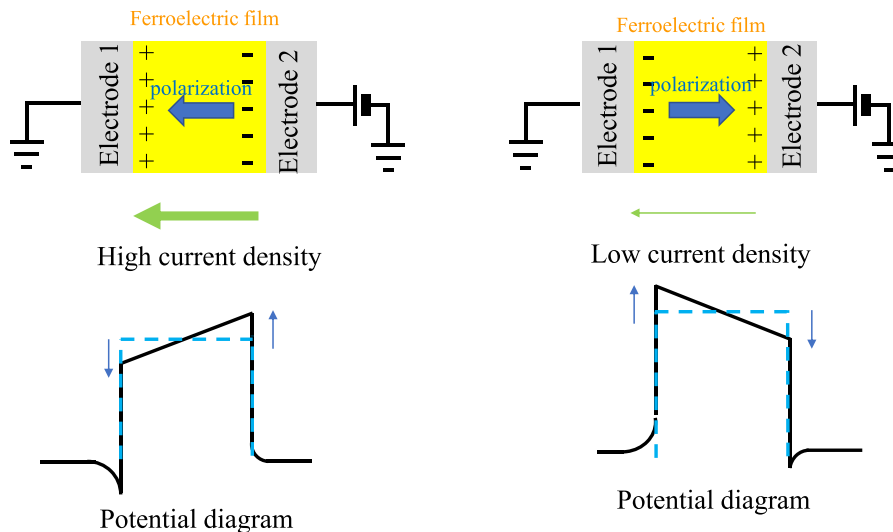


Fig. 16 Schematic illustration of the operation principle of FTJ. Tunneling barrier height and thus tunneling electroresistance can be modulated by applying voltage and switching polarization in the ferroelectric layer. Reproduced from Kobayashi, M., Tagawa, Y., Mo, F., Saraya, T., Hiramoto, T., 2018a. Ferroelectric HfO_2 tunnel junction memory with high TER and multi-level operation featuring metal replacement process. IEEE J. Electron Devices Soc. 7, 134–139. doi:10.1109/JEDS.2018.2885932.

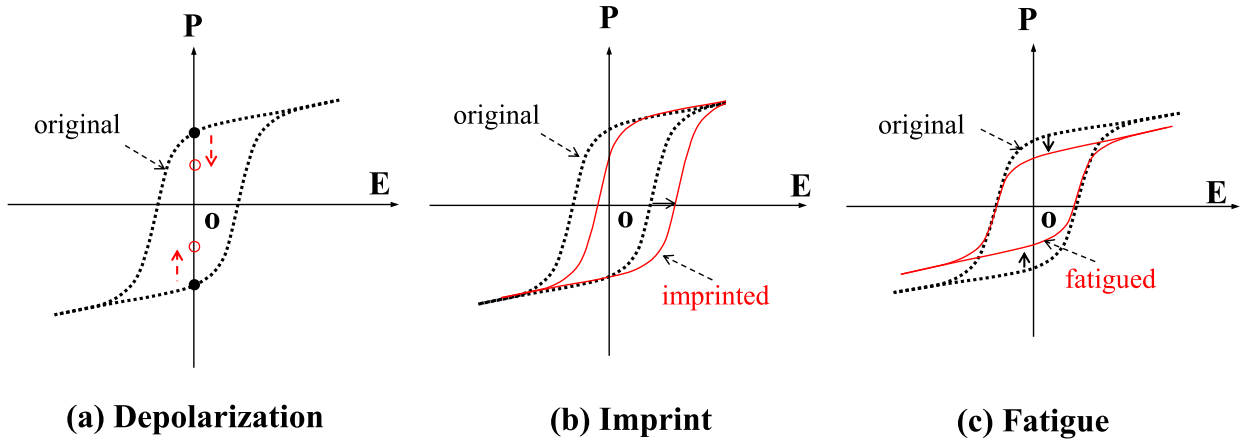


Fig. 17 Degradation models of ferroelectric capacitor: (a) depolarization; (b) imprint; and (c) fatigue.

where ε_f , C_d and C_f , are permittivity of ferroelectric film, dielectric capacitance, and ferroelectric capacitance, respectively. When areas both of the ferroelectric and the dielectric capacitor are same, like a FeFET gate structure, Eq. (29) is expressed as;

$$E_{dep} = \frac{P}{\varepsilon_f} \frac{1}{\left(\frac{\varepsilon_d}{\varepsilon_f} \frac{t_f}{t_d} + 1\right)} \quad (30)$$

where ε_d , t_f , and t_d are a permittivity of dielectric film, a thickness of ferroelectric film, and a thickness of dielectric film, respectively. Therefore, FM has the larger $\frac{C_d}{C_f}$ ratio or $\frac{\varepsilon_d}{\varepsilon_f} \frac{t_f}{t_d}$, the smaller depolarization field appears in ferroelectric film. In the FC integrated in the capacitor-type FRAM, a degraded layer, existing near the interface between a ferroelectric film and an electrode, works as a dielectric layer and degrades memory retention. It also should be noted that depolarization field should arise from incomplete compensation of the ferroelectric polarization even in the absence of dielectric layer (Mehta *et al.*, 1973).

Imprint

Imprint is observed as hysteresis shifts from the original position as shown in Fig. 17 (b). For example, P-E hysteresis shifts to the positive direction after storing the “1” state. Various origins inducing this type of degradation have been proposed, for example, charged defects such as oxygen vacancy or its related defects (Ishibashi and Takagi, 1971; Mihara and Araujo, 1993; Tagantsev *et al.*, 2004; Fengler *et al.*, 2016) or ferroelectric domain pinning (Alexe *et al.*, 2001). To improve in the degradation of FC by imprint, it has been reported that doping to ferroelectrics, for example, Nb doping into PZT (Souza *et al.*, 2004; Zhao *et al.*, 2016). And also using oxide electrode, for example, IrO₂ (Nakamura *et al.*, 1994), SrRuO₃ (Stolichnov *et al.*, 1999), LaSrCoO₃ (Ramesh *et al.*, 1993) instead of noble metal has been reportedly effective.

Measurement of Retention and Imprint

For commercialized capacitor type FRAM, a testing procedure has been established (Rodriguez *et al.*, 2010). A retention test checks the ability of the FC to retain the initial stored data (“same state” or SS). If the FC is degraded by depolarization, the data reading operation may fail in this test. An imprint test checks the ability of a FC to rewrite the stored data as opposite data (“opposite state” or OS), for example, writing and storing “1” corresponding to the position “1” as depicted in Fig. 1, and then rewriting the stored “1” as “0” corresponding to the position “0” in Fig. 1. If the P-E hysteresis of the FC shifts, the reading operation of the rewritten data may fail in this test, because rewriting the opposite data becomes difficult due to an increase in E_c . A test procedure for retention and imprint is shown in Fig. 18. In this procedure, the baking temperature is set up according to the activation energy of degradation, which is previously evaluated according to the Arrhenius equation before baking. We carry out those tests on the testing arrays from 516 Kb to a few Mb and obtain bit distributions. Fig. 19. shows a schematic “0” and “1” bit distribution. A sensing margin, a voltage between the highest sensing voltage of “0” and lowest sensing voltage “1”, as shown in the Fig. 19 generally decreases with baking time due to degradation of ferroelectric film. The device lifetime is determined by the time when this margin going to the sensing limit.

Fatigue, Wake up, and Their Measurements

Fatigue is observed as hysteresis shrinks from the original during iteration of polarization reversal as shown in Fig. 17(c). Origin of this degradation has been investigated by many researchers for long time. Typical models proposed until now are ferroelectric domain wall pinning (Wang *et al.*, 1995; Huang *et al.*, 2017), oxygen vacancy (Scott and Dawber, 2000; Fengler *et al.*, 2016), dielectric interlayer existing between ferroelectric and electrode (Suenaga *et al.*, 2000), and local phase decomposition (Lou *et al.*, 2006). A fatigue or a writing endurance test checks the read/write function of FC after repetitions of polarization reversal. A test procedure of fatigue is shown in Fig. 20. The writing endurance of commercialized capacitor type PZT based FRAMs is from 10^{13} to 10^{15} , which is

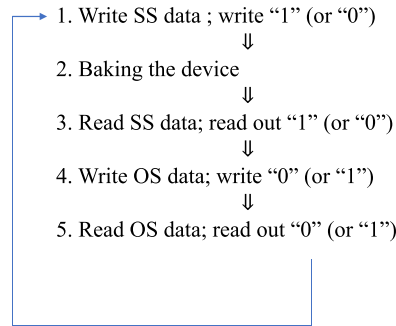


Fig. 18 A retention and imprint test procedure.

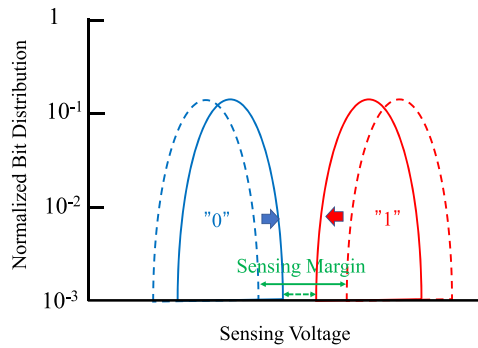


Fig. 19 A schematic normalized bit distribution before and after retention and imprint test.

more than 10^8 – 10^{10} times larger than that of FLASH memory. In the HfO_2 -Fe based FeFET, Tan *et al.* (2021) demonstrated the writing endurance of 10^{10} on their HfZrO_2 based FeFET incorporated with a high-k layer measured by gate voltages of ± 3 V. It is worth commenting about “retention after fatigue” which means a retention ability of fatigued FM (Hadnagy *et al.*, 2001). This test category is also important for practical use of FM, which assesses the degradation by depolarization and imprint on the previously fatigued samples, because FRAM often needs to store information for long time after repeatedly rewriting.

During measurement of fatigue in HfO_2 -Fe, “wake up” has been often observed as an increase in P_r (Mueller *et al.*, 2012). Before the first report of the wake-up phenomenon in HfO_2 -Fe, similar “wake-up” phenomenon has been already reported in SBT (Okamura *et al.*, 2000) and in PZT (Kartawidjaja *et al.*, 2007). While wake up was observed as an increasing P_r and an improvement in P-E hysteresis in the case of PZT and SBT, “wake-up” was observed as an enhancement in P and a shift of negative coercive field (Zhou *et al.*, 2013) in case of the HfO_2 -Fe. Various investigation has suggested that oxygen vacancy should relate to this phenomenon (Zhou *et al.*, 2013; Starschich *et al.*, 2016; Kashir *et al.*, 2021). Kashir *et al.* (2021) reported their achievement for “a nearly wake-up free” HfZrO_2 ferroelectric memory by reduction of carbon contamination and oxygen defects.

Soft Breakdown and TDDB

Ferroelectric films need robustness against dielectric breakdown when using in semiconductor devices. Electrons or holes tunneling through a dielectric film generate defects eventually resulting in a type of dielectric breakdown called “soft-breakdown.” We estimate the soft-breakdown life time by means of a time-dependent-dielectric breakdown (TDDB) measurement method. The TDDB method measures electrical breakdown time by imposing a DC or sometimes an AC voltage on a ferroelectric film. Mechanisms of the soft breakdown has been well investigated for SiO_2 , used as a gate insulator of FET (Stathis, 2001), and PZT (Chen *et al.*, 1996; Wang *et al.*, 2017). Soft breakdown about HfO_2 -Fe is one of the serious problems because the HfO_2 -Fe with thickness of 10 nm or less needs to be used due to its large E_c . Wei *et al.* (2020) investigated the failure mechanism of the FM using $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$, they found that annealing temperature of ferroelectric film has a large impact on the initial defect concentration, and the breakdown paths take place mainly in the amorphous region. Chen *et al.* (2020) reported that TDDB life time was improved for their MFS structure by NH_3 plasma cleaning on the Si surface just before the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ deposition. They estimated the TDDB life time to be 10 years with 0.01% failure rate at gate voltages of 1 by extrapolating their data.

Soft breakdown problem seems more crucial for the HfO_2 -Fe FTJ memory because it needs to increase the “On” current in order to increase On-Off ratio. Yamaguchi *et al.* (2020) have developed FTJ memory with decoupled structure of ferroelectric stored layer and tunneling layers (HfO_2 -Fe/ SiO_2 inter layer) aiming to application for the in-memory computing). They investigated TDDB life time and attributed the soft-breakdown on their FTJ memory to defect generation in the SiO_2 inter layer. They optimized learning algorithm to satisfy endurance requirements for their in-memory computing application.

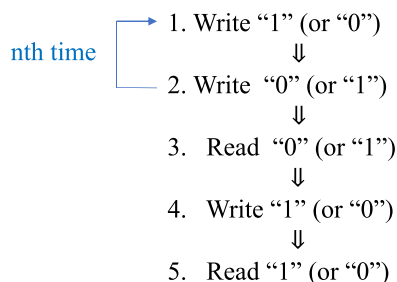


Fig. 20 A fatigue test procedure.

Future Directions

FM was commercialized as FRAM with memory density of several hundreds of Kb for the first time in the late 1990s and has evolved to FRAM with memory density of several Mb and much higher reliability. Although it has been expected to become a “dream memory” to alternate all of the semiconductor memories, it has been only applied to specific devices due to its inferior scalability. However, FM have attracted a lot attention again by discovery of $\text{HfO}_2\text{-Fe}$ in 2011 because it is expected to overwhelm the scalability problems thanks to its excellent compatibility with CMOS production process. If high reliability of $\text{HfO}_2\text{-Fe}$ is proven, FM using $\text{HfO}_2\text{-Fe}$ will become a real “game changer.” Furthermore, 3D NAND FeFET and FTJ memory, which many researchers have been striving for their commercialization, are promising to realize super high density NVM. Neuromorphic memories and in-memory computing using FM are potentially become a main stream memory leading “More than Moore’s” technology.

Conclusions

Ferroelectric memory is a non-volatile memory using ferroelectric materials, including FRAM, FeFET and FTJ memory, with an excellent electric properties of high writing speed, high rewriting endurance, and low energy consumptions. It has been only used in the specific region because of its relatively low memory density. Recent discovered HfO_2 based ferroelectric material potentially has been expected to realize the high density ferroelectric memory because of its scalability due to full compatibility with CMOS production process.

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Lead-Free Piezoelectric Ceramics

Jianguo Zhu, Jie Xing, Zhi Tan, Lixu Xie, Yuan Cheng, Manjing Tang, and Ning Chen, College of Materials Science and Engineering, Sichuan University, Chengdu, China

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Abstract

The lead-free piezoelectric ceramics have attracted great attention all over the world for meeting the requirements of environmental protection and sustainable development of human society in recent years. Lead-free piezoelectric ceramics not only have satisfactory piezoelectric properties, but also contain no lead and have good environmental compatibility. The compelling physical properties of lead-free piezoelectric ceramics were highlighted and their state-of-the-art progress was summarized. The unique advances in lead-free piezoelectric ceramics, along with the main physical mechanisms of high piezoelectricity, including phase boundaries, domain configurations, and grain size effects, were also summarized. In particular, the applications of lead-free piezoelectric ceramics were introduced and evaluated. Finally, challenge and perspective are featured on the basis of their current developments.

Introduction

Piezoelectric materials that can realize the mutual conversion of mechanical and electric energy have been widely applied in sensors, actuators, transducers, and energy harvesters (Jaffe *et al.*, 1971; Lines and Glass, 1977; Uchino, 2000) owing to their outstanding piezoelectric, mechanical and acoustic properties. There are two conditions for ceramics to have piezoelectricity: one is that the grains of ceramics are ferroelectric; the other is that they need to be processed by a strong dc electric field (artificial polarization). Piezoelectric ceramics are different with piezoelectric crystals. Piezoelectric crystals are divided two kinds: ferroelectric piezoelectric crystals and non-ferroelectric piezoelectric crystals. This sentence is a little ambiguous. I think.

The piezoelectricity of ceramics was first found in BaTiO₃. However, pure BaTiO₃ ceramics are difficult to be sintered, and the Curie temperature T_C is not high (about 120°C) (Bechmann, 1956). Lead zirconate titanate [Pb(Zr_xTi_{1-x})O₃, PZT] invented in the 1950s (Shirane and Takeda, 1952; Jaffe *et al.*, 1954) is the most widely used piezoelectric ceramic. Up to now, many lead-based piezoelectric ceramics, such as PZT, Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) (Ye, 1996; Park and Shrout, 1997; Zhang *et al.*, 2015b), Pb(Zn_{1/3}Nb_{2/3})O₃-PT (PZN-PT) (Kuwata *et al.*, 1981; Park and Hackenberger, 2002), and so on, have been widely applied in many fields (Cross, 1987; Uchino, 2000), and occupied most of the market share. Lead-based piezoelectric ceramics have a higher Pb content (~60 wt%). It will cause serious pollution to the environment and great damage to human health during production, preparation, use and disposal. Many countries have enacted legislation to prohibit the use of lead-containing electronic materials.

At present, the piezoelectric ceramic materials that have been studied and put into application mainly include perovskite structure, tungsten bronze structure, bismuth layered structure ferroelectrics (BLSFs) and perovskite like structure (PLS), among which the perovskite group is the most important and thus the most widely studied (Damjanovic, 1998; Fu and Cohen, 2000; Akdogan *et al.*, 2005; Wu *et al.*, 2018b; Li *et al.*, 2018a). The performance comparison of these types of piezoelectric materials is shown in Table 1. The relationship between the piezoelectric constant d_{33} and of different piezoelectric ceramics is shown in Fig. 1.

The lead-free piezoelectric ferroelectric ceramics have attracted great attention all over the world for meeting the requirements of environmental protection and sustainable development of human society in recent years (Xiao, 1998; Takenaka and Nagata, 2005; Zhu *et al.*, 2007; Rödel *et al.*, 2009; Wu *et al.*, 2015). Lead-free piezoelectric ceramics are a kind of new piezoelectric ceramics that not only have satisfactory piezoelectric properties, but also contain no lead and have good environmental compatibility.

According to the structure classification, lead-free piezoelectric ceramics mainly have the following four categories, as shown in Fig. 2.

Background/Fundamentals

Perovskite Structure

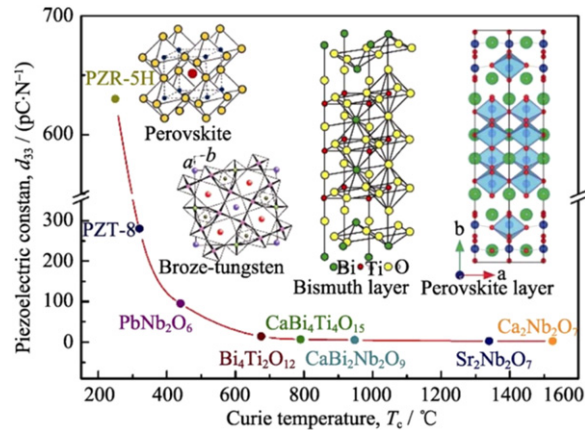
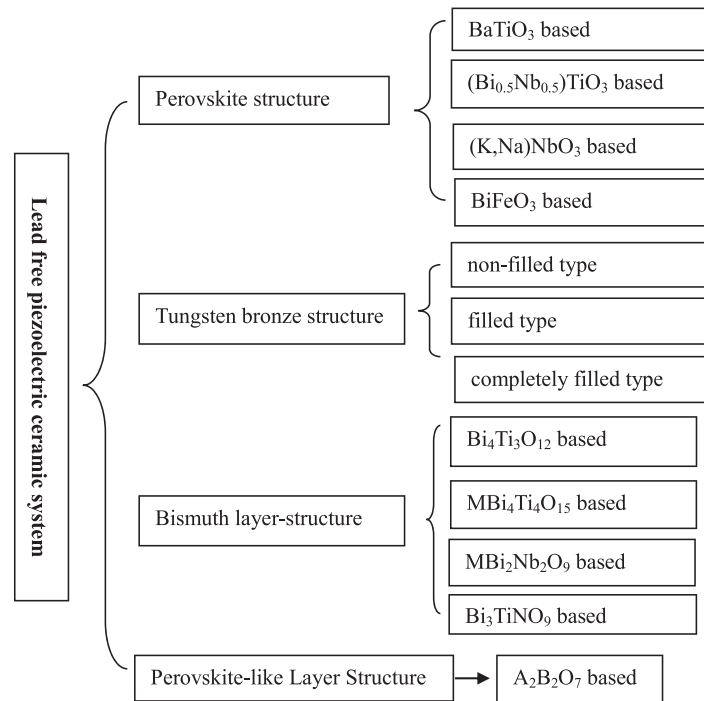
A typical ABO₃-type perovskite structure is shown as Fig. 3, taking BaTiO₃ as an example. The larger A-site cations are located at the apex position, while the smaller B-site cations are located at the body-centered position and oxygen ions occupied the face-centered position. It hereby forms an oxygen octahedron around the B-site cation and a truncated oxygen hexahedron around A-site cation (Bhalla *et al.*, 2000). Ti⁴⁺ ions occupy the B-site while Ba²⁺ ions occupy the A-site. Many ferroelectrics, such as BaTiO₃, (Bi_{0.5}Na_{0.5})TiO₃, and (K_{0.5}Na_{0.5})NbO₃, are perovskite structure.

The general chemical formula of the composite perovskite type multi-component oxides can generally be written as (A₁, A₂, ... A_k) (Smolensky, 1961) (B₁, B₂, ... B_l)O₃. In this case, the ions at A and B positions should meet the following conditions:

$$\sum_{i=1}^k \chi_{Ai} = 10 < \chi_{Ai} \leq 1;$$

Table 1 The electrical properties of practical high T_c piezoelectric ceramics

Name	Structure	T_c ($^{\circ}\text{C}$)	ϵ_r	d_{33} (pC/N)	k_{33}	Q_m	ρ ($10^{10}\Omega \cdot \text{cm}$)	E_c (kV/cm)
Pb(Zr,Ti)O ₃	perovskite	330	1800	417	0.73	75	100	10–12
(Ba,Pb)Nb ₂ O ₆	tungsten bronze	400	300	85	0.30	15	1	–
PbTiO ₃	perovskite	490	190	56	0.45	1300	10	>40
Bi ₄ Ti ₄ O ₁₅	bismuth layered	~600	140	18	0.15	100	1000	>50
(Bi _{0.5} Na _{0.5})TiO ₃	perovskite	315	300	70	0.40	240	–	73
LiNbO ₃	corundum	1150	25	6	0.23	–	1	200
La ₂ Ti ₂ O ₇	perovskite like	1458	–	2.6	–	–	–	–

**Fig. 1** The relationship of Curie temperature and the piezoelectric constant d_{33} of different piezoelectric materials. Reproduced from Zhou, Z.Y., Chen, T., Dong, X.L., 2018. Research progress of perovskite layer structured piezoelectric ceramics with super high Curie temperature. Journal of Inorganic Materials 33 (3), 251–258, with the permission of Shanghai Institute of Ceramics.**Fig. 2** Lead-free piezoelectric ceramic system.

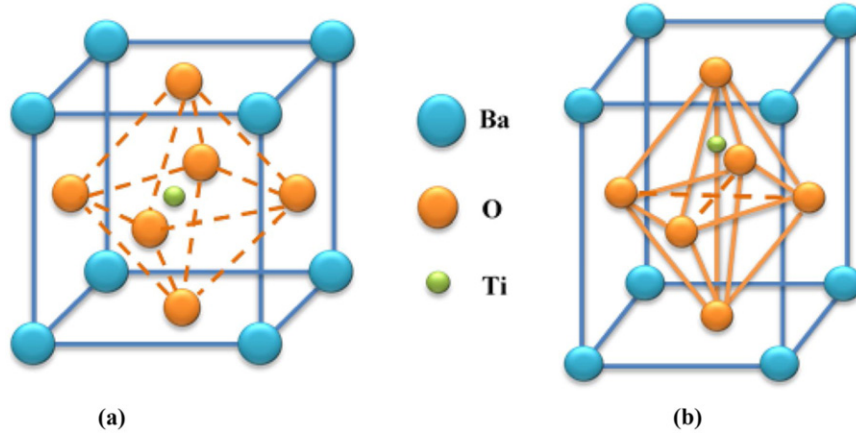


Fig. 3 Schematic illustration of the perovskite structure of BaTiO₃ (a) Cubic lattice (above Curie temperature, >120°C) (b) Tetragonal lattice (below Curie temperature, <120°C).

$$\sum_{j=1}^l \chi_{Bji} = 1 \quad 0 < \chi_{Bj} \leq 1$$

$$\sum_{i=1}^k \chi_{Ai} n_{Ai} = \bar{n}_A; \sum_{j=1}^l \chi_{Bj} n_{Bj} = \bar{n}_B; \bar{n}_A + \bar{n}_B = 6 \quad (1)$$

$$\bar{r}_A = \sum_{i=1}^k r_{Ai} \chi_{Ai} \quad \bar{r}_B = \sum_{j=1}^l r_{Bj} \chi_{Bj}$$

where, χ_{Ai} and χ_{Bj} are the mole fraction of each ion at position A and B, r_{Ai} and r_{Bj} are the ionic radius of each ion at position A and B. $\bar{r}_A$ and $\bar{r}_B$ are the average radii of the ions at positions A and B. The conditions for the formation of composite perovskite structure are as follows (Goldschmidt, 1926):

$$t = \frac{(\bar{r}_A + r_O)}{\sqrt{2}(\bar{r}_B + r_O)} \quad 0.88 \leq t \leq 1.1 \quad (2)$$

where $\bar{r}_A$, $\bar{r}_B$, r_O is the A-site ion average radius, B-site ion average radius and oxygen ion radius, respectively. When $t = 0.88 - 1.09$, there is a high probability to form a stable perovskite structure and the crystal structure tends to be tetragonal; when $t > 1$ it tends to be rhombohedral, or orthorhombic when $t < 1$.

The composite perovskite oxides are prepared by the solid solution method. At this time, the A and B sites are composed of two or more elements with different atomic valences. The average atomic valence of A site is +2 and B site is +4.

Most ferroelectric materials undergo a structural phase transition from a high temperature paraelectric phase into a low temperature ferroelectric phase. The paraelectric phase always has a higher symmetry than the ferroelectric phase. The temperature of the phase transition is called as the Curie temperature (T_C). Different ferroelectric materials have different values of T_C , which can be either lower than liquid nitrogen temperature or higher than 1000°C. For a given material (composition), the T_C is closely related to microstructure (grain size and distribution, density, porosity and pore size and distribution, and impurity, and so on). The phase transition of ferroelectrics often leads to strong anomalies in dielectric, elastic, thermal and other properties of the materials, among which dielectric variation before and after a phase transition is the most significant and thus usually used as an indication of phase transition.

At room temperature, BiFeO₃ has rhombic distorted perovskite structure, the space group is R_{3C} , the lattice constant is $a = b = c = 5.633 \text{ \AA}$ and $\alpha = \beta = \gamma = 59.4^\circ$, and the lattice structure is shown in Fig. 4. Compared with the cubic perovskite structure, with the surrounding oxygen ions as the coordinates, Bi ions will move along the [111] direction, while the oxygen octahedron will twist around the [111] axis, resulting in polarization along the [111] direction, and its ferroelectric phase transition occurs in $T_C \sim 1103\text{K}$. It is predicted theoretically that the saturated electrode can reach $100 \mu\text{C}/\text{cm}^2$ at room temperature (Wang *et al.*, 2003).

Tungsten Bronze Structure

Tungsten bronze structure can be divided into many types, among which the tetragonal tungsten bronze structure is the most common, widely studied and used. Tungsten bronze structure ferroelectric compounds are the second class of ferroelectric compounds next only to perovskite class compounds, and the general chemical formula of the tungsten bronze structure is $A_6B_{10}C_4O_{30}$, where the A site and the B site can be occupied by only one ion, or by two or more ions. So the chemical formula of the tungsten bronze structure can be rewritten as $[(A1)_2(A2)_4C_4][(B1)_2(B2)_8]O_{30}$ (Jamieson *et al.*, 1969). The tetragonal tungsten bronze unit cell is composed of a lattice network formed by connecting 10 oxygen octahedrons BO_6 with a common vertex.

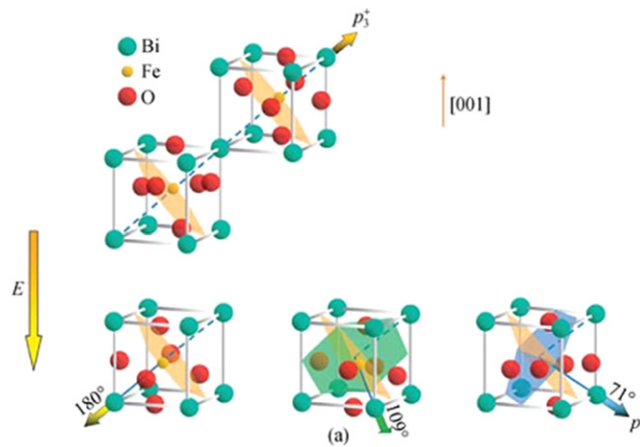


Fig. 4 Structure diagram of BiFeO_3 .

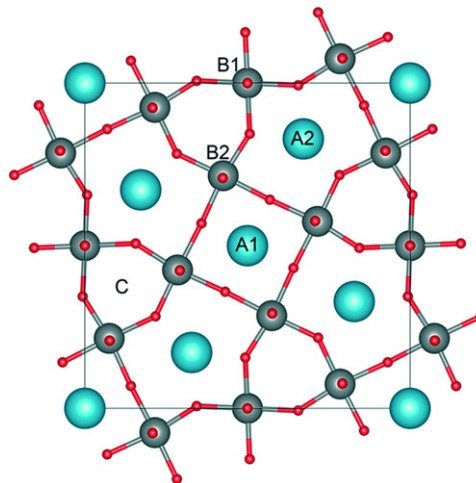


Fig. 5 $[001]$ projection of the prototype tungsten bronze structure illustrating the interstices described by the corner sharing octahedral.

Different from perovskite structure, these oxygen octahedrons have different central symmetry and have inconsistent orientation in the plane perpendicular to the quadruple axis. The B site can be divided into B_1 and B_2 according to its symmetry difference, and there is little difference between the two. The B site is usually occupied by tetravalent and pentavalent oxygen ions with a smaller ion radius, such as Zr^{4+} , Ti^{4+} , Ta^{5+} , Nd^{5+} and so on. At the same time, the network structure formed by the co-top connection of oxygen octahedrons also produces three different types of gaps, A1, A2 and C. A1 is a large pentagonal gap with a coordination number of 15; A2 is a quadrilateral gap with a coordination number of 12; C is a triangular gap with a coordination number of 9. **Fig. 5** shows the projection of a tetragonal tungsten bronze structure unit cell on the (001) plane. Among them, A1 and A2 can be replaced by monovalent cations (such as K^+ , Na^+ and Rb^+), divalent cations (such as Ba^{2+} , Sr^{2+} , Ca^{2+} , etc.) or trivalent cations (such as La^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , etc.), while the C site can only be occupied by cations with a smaller radius, such as Li^+ , Be^{2+} and Mg^{2+} . The existence of the unequal A-site, B-site and C-site in the crystal structure greatly enhances the freedom degree of structural modulation, and provides a basis for the synthesis of tungsten bronze materials with flexible structures and exhibiting rich properties.

Tungsten bronze structural materials can be divided into three types: non-filled type, filled type and completely filled type according to the different filling levels of the A-site filling ions. Among them, when the A1, A2 sites are not all filled with cations and the C site is completely empty, it is a non-filled tungsten bronze, such as $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN) (Jamieson *et al.*, 1968); when the A1, A2 sites are all filled with cations and the C site is completely empty, it is a filled tungsten bronze, such as $\text{Ba}_6\text{Ti}_2\text{Nb}_8\text{O}_{30}$ (Stephenson, 1965) and $\text{Sr}_{2-x}\text{Ca}_x\text{NaNb}_5\text{O}_{15}$ (Neurgaonkar *et al.*, 1988); when all A1, A2 and C sites are filled with cations, it is a completely filled tungsten bronze, such as $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ (KLN) (Uematsu and Koide, 1970).

A large number of compounds crystallize with tungsten bronze structure, with widely varying characteristics depending on the number of sites occupied and on the size and charge of the metal atoms.

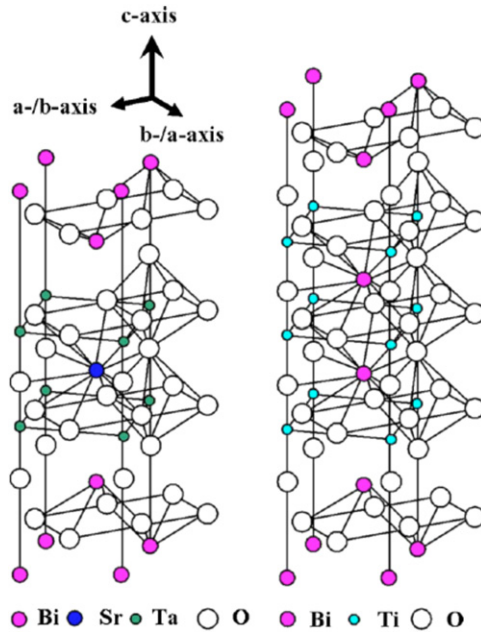


Fig. 6 Schematic illustration of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (left, $m = 2$) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (right, $m = 3$) crystal structures, which show a half unit cell along the c axis. Reproduced from Watanabe, T., Funakubo, H., 2006. Controlled crystal growth of layered-perovskite thin films as an approach to study their basic properties. Journal of Applied Physics 100, 051602, with the permission of AIP Publishing.

Table 2 Lead-free BLSFs (Ln: lanthanoid)

m	1	2	3	4	5
Materials	$\text{Bi}_2\text{VO}_{5.5}$ Bi_2MoO_6 Bi_2WO_6	$\text{SrBi}_2\text{Ta}_2\text{O}_9$ $\text{CaBi}_2\text{Ta}_2\text{O}_9$ $\text{BaBi}_2\text{Ta}_2\text{O}_9$ $\text{SrBi}_2\text{Nb}_2\text{O}_9$ $\text{CaBi}_2\text{Nb}_2\text{O}_9$ $\text{BaBi}_2\text{Nb}_2\text{O}_9$ $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ $\text{Bi}_3\text{TiTaO}_9$ $\text{Bi}_3\text{TiNbO}_9$	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ $(\text{Bi}_{4-x}\text{Ln}_x)\text{Ti}_3\text{O}_{12}$ $\text{Bi}_{4-x/3}\text{Ti}_{3-x}\text{V}_x\text{O}_{12}$ $\text{Bi}_{4-2x/3}\text{Ti}_{3-x}\text{W}_x\text{O}_{12}$ $(\text{Bi},\text{Ln})_4(\text{Ti},\text{V})_3\text{O}_{12}$ $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{MnO}_{12-x}$ $(\text{Bi}_{4-x}\text{Sr}_x)(\text{Ti}_{3-x}\text{Nb}_x)\text{O}_{12}$ $(\text{Bi}_{4-x}\text{Ba}_x)(\text{Ti}_{3-x}\text{Nb}_x)\text{O}_{12}$	$\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ $\text{K}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$	$\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$
m	1, 2		2, 3	3, 4	∞
Materials	$\text{Bi}_2\text{WO}_6 - \text{Bi}_3\text{Ti}_{1.5}\text{W}_{0.5}\text{O}_9$ $\text{Bi}_2\text{WO}_6 - \text{Bi}_3\text{TiNbO}_9$ $\text{Bi}_2\text{WO}_6 - \text{Bi}_2(\text{Bi}_{0.5}\text{Na}_{0.5})\text{NbO}_9$ $\text{Bi}_2\text{WO}_6 - \text{Bi}_3\text{TaTiO}_9$		$\text{Bi}_3\text{Ti}_{1.5}\text{W}_{0.5}\text{O}_9 - \text{Bi}_4\text{Ti}_3\text{O}_{12}$ $\text{Bi}_3\text{TiNbO}_9 - \text{Bi}_4\text{Ti}_3\text{O}_{12}$ $\text{Bi}_3\text{TiTaO}_9 - \text{Bi}_4\text{Ti}_3\text{O}_{12}$ $\text{SrBi}_2\text{Nb}_2\text{O}_9 - \text{Bi}_4\text{Ti}_3\text{O}_{12}$ $\text{BaBi}_2\text{Nb}_2\text{O}_9 - \text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Bi}_4\text{Ti}_3\text{O}_{12} - \text{SrBi}_4\text{Ti}_4\text{O}_{15}$ $\text{Bi}_4\text{Ti}_3\text{O}_{12} - \text{BaBi}_4\text{Ti}_4\text{O}_{15}$ $\text{Bi}_4\text{Ti}_3\text{O}_{12} - (\text{Na}_{0.5}\text{Bi}_{0.5})\text{Bi}_4\text{Ti}_4\text{O}_{15}$	SrTiO_3 BaTiO_3

Note: Reproduced from Watanabe, T., Funakubo, H., 2006. Controlled crystal growth of layered-perovskite thin films as an approach to study their basic properties. Journal of Applied Physics 100, 051602, with the permission of AIP Publishing.

Bismuth Layered Structure Ferroelectrics (BLSFs)

Bismuth layered structure ferroelectrics (BLSFs) with representative Aurivillius structure (Aurivillius, 1950a,b, 1951), which can be described as the intergrowth of $(\text{Bi}_2\text{O}_2)^{2+}$ layers and $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ perovskite-like slabs, where A-site allows cations with low valence, large radius and dodecahedral coordination or the mixture of these cations (such as Na^+ , Ca^{2+} , Ce^{4+} , etc.), B-site allows transition cations with octahedral coordination or the mixture of these cations (such as Sc^{3+} , Ti^{4+} , Ta^{5+} , etc.) and m is the number of octahedral BO_6 in perovskite like slabs, are a potential candidate for high-temperature sensors, because of its low dielectric loss, high T_C and superior thermal stability (Isupov, 2006). The typical BLSFs structures are shown as Fig. 6.

Almost all BLSFs have orthorhombic symmetry at room temperature (that of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is strictly monoclinic). A variety of over 50 materials with different m numbers typically ranging from 1 to 5, or a combination of them, have been reported and are

considered to be ferroelectrics. Depending on the m number, the c -axis lattice parameter changes at intervals of about 8 Å, which corresponds to two perovskite units. The a/b axis is parallel to the diagonal of the pseudoperovskites, so that the a/b axis lattice parameters are approximately root two times the typical lattice parameters of perovskite materials, 4 Å. Table 2 listed several typical lead-free BLSF ceramics.

However, the rotation of BLSFs spontaneous polarization (P_s) is limited in two-dimensional orientation and the coercive fields of BLSFs are high, which make polarization difficult and relatively low piezoelectric coefficient (d_{33}). Table 3 shows the T_C and d_{33} with different m of some BLSFs. Currently, the following methods are commonly used to improve the properties of bismuth layered piezoelectric ceramics:

- (1) Chemical doping including A site substitution, B site substitution or A, B co-substitution, and A site substitution ions are generally alkali metal ions (Li^+ , Na^+ , K^+), rare earth ions (La^{3+} , Ce^{4+} , Nd^{5+} , etc.) or their compound ions, B site substitution ions are generally Mn^{2+} , Co^{3+} , W^{6+} , etc;
- (2) Forming symbiotic structure with another bismuth layered compound;
- (3) Forming solid solution with perovskite structure compounds;
- (4) Textured technology related to heat treatment, directional solidification and TGG, etc. However, the high cost and complex process of grain orientation make it difficult to be used in the industrial production of bismuth layered piezoelectric ceramics. In recent years, $\text{Bi}_2\text{O}_2^{2+}(\text{AB}_2\text{O}_7)^{2-}$ ($m = 2$) based, $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_2\text{B}_3\text{O}_{10})^{2-}$ ($m=3$) based and $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_3\text{B}_4\text{O}_{13})^{2-}$ ($m=4$) based piezoelectric materials can meet the requirements of high temperature piezoelectric sensors with high Curie temperature and high d_{33} are mainly reported.

Perovskite-Like Structure

Perovskite-like structure (PLS) materials, a general molecular formula of $\text{A}_n\text{B}_n\text{O}_{3n+2}$, have attracted extensive attention in high temperature application fields (Yan *et al.*, 2009), including automation, aerospace, petroleum, geological exploration, the power generation industry, and so on, due to their high T_C and stable electrical properties at high temperature regions. The PLS is characterized by BO_6 octahedra shared at the corner and 12-coordinated A cations, in which the perovskite-like layers are separated by oxygen ions (Lichtenberg, 2001).

In the general formula $\text{A}_n\text{B}_n\text{O}_{3n+2}$, n is the number of oxygen octahedral layers in a lattice, usually depending on the size of the cation, and the layers are linked by A cations at their boundaries, as shown in Fig. 7. When $n = 2, 3, 5, 6$ or greater than 6, ferroelectric properties are rarely reported, $n = 3, 5$ and 7 are centrosymmetric structures, while $n = 4$ and 6 are non-centrosymmetric structures. When $n = 4$, the compound formula can be simplified to $\text{A}_2\text{B}_2\text{O}_7$ -type structure; and when $n = \infty$, it can be simplified to ABO_3 -type perovskite structure. Therefore, the PLS can be understood as the layered structure formed by cutting the perovskite structure along a specific direction.

Main Body

Perovskite Structure Based Lead –Free Piezoceramics

BaTiO₃-based lead –free piezoceramics

BaTiO₃ piezoelectric ceramics

The T_C of BaTiO_3 is 120°C. Above 120°C, BaTiO_3 has a cubic structure and is a paraelectric phase. When the temperature drops from high temperature to 120°C, the BaTiO_3 structure would be changed from cubic structure to tetragonal structure. At this time, the c -axis is slightly elongated, $c/a \approx 1.01$, and the crystal has spontaneous polarization along the c -axis, which is a ferroelectric phase (Megaw, 1945). The spontaneous polarization is $26 \times 10^{-2} \text{ C/m}^2$ at room temperature. When the temperature drops below -5°C , the lattice structure changes to orthorhombic system (three mutually perpendicular a , b , c axes), and the spontaneous polarization direction changes to (011) (Lines and Glass, 1977). Generally, the a -axis of orthorhombic crystal system is taken in the polarization direction, the b -axis of orthorhombic crystal system is taken in the (011) direction of the adjacent cube and perpendicular to the a -axis, and the c -axis is taken in the direction perpendicular to the a -axis and b -axis and is parallel to the original cube edge (100). If the temperature continues to drop to -80°C , the lattice structure becomes triangular symmetry. At this time, the three edges of the unit cell are equal, $a = b = c$, and the angle $\alpha = 82.92^\circ$. The spontaneous polarization is along the (111) direction of the original cubic system. Fig. 8 shows the cell change of BaTiO_3 when the temperature changes.

The reason why the properties of BaTiO_3 ceramics change greatly with temperature is that the Curie temperature T_C (about 120°C) and the second phase transition temperature (about -5°C) are near room temperature. Because the properties of piezoelectric ceramics are unstable near the phase transition temperature, when used as piezoelectric materials, this phenomenon causes the instability of piezoelectric constants. Adding a few percent moles of ABO_3 type compound to form solid solutions makes the phase transition point move to the low temperature direction. At the same time, it causes the rise of T_C and the increase of E_C , so stable piezoelectric materials can be obtained. Adding a few percent moles of CaTiO_3 and PbTiO_3 to BaTiO_3 to form solid solutions can improve its temperature stability and time stability.

BaTiO₃ – based piezoelectric ceramics

Liu and Ren (2009) proposed a pseudo-binary ferroelectric $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (abbreviated as $(1-x)\text{BZT}-x\text{BCT}$) system or BCZT, similar to $\text{PbZrO}_3\text{-PbTiO}_3$, achieving surprisingly high piezoelectric properties (piezoelectric constant $d_{33} \sim 620$ pC/N and piezoelectric strain constant $d_{33}^*(dS/dE) \sim 1140$ pm/V), at its morphotropic phase boundary (MPB) ($x = 0.5$). Its superior properties even exceed that of many soft PZTs. Thus, this discovery caused BT-based systems, especially the BZT–BCT systems to attract extensive attention.

In 2013, the phase diagram of BZT–BCT was reinvestigated using high-resolution synchrotron X-ray powder diffraction (Keeble *et al.*, 2013), which indicated that an intermediate orthogonal phase (O phase) as the bridging phase existed between the rhombohedral phase (R phase) and tetragonal phase (T phase), as shown in Fig. 9.

Based on the design idea of triple-point “MPB”, large d_{33} values of 360–680 pC/N can be also achieved in $(\text{Ba,Ca})(\text{Ti,Sn})\text{O}_3$ ceramics (169-Yan, 2020). Wang *et al.* (2020) prepared the Sn doped BT ceramics, and they found that when $x = 0.11$, the BTS_x had the rather high piezoelectric properties: $d_{33} \sim 1120$ pC/N, $k_p \sim 0.58$, and $T_C \sim 85^\circ\text{C}$, respectively. This giant d_{33} value of ~ 1120 pC/N is about twice that of other BT-based, KNN-based systems and soft PZTs encompassing only R + T or R + O + T mixed phases, such as 620 pC/N for BTZ-0.5BCT , 570 pC/N for $0.95\text{K}_{0.6}\text{Na}_{0.4}\text{Nb}_{0.965}\text{Sb}_{0.035}\text{O}_3-0.02\text{BaZrO}_3-0.03\text{Bi}_{0.5}\text{K}_{0.5}\text{HfO}_3$ and 590 pC/N for ultrasoft PZT5H, which is currently the highest value reported in lead-free materials.

(Bi,Na)TiO₃-based lead –free piezoceramics

Phase transition order

The $(\text{Bi,Na})\text{TiO}_3$ (BNT) was discovered by Smolensky *et al.* (1960), which is a A-site disordered relaxor ferroelectric. BNT exhibits a large spontaneous polarization P_r of ~ 40 $\mu\text{C}/\text{cm}^2$ at room temperature, which is attributed to the hybridization between Bi 6s and O 2p orbitals (Zhou *et al.*, 2021). A giant field-induced strain is found in BNT-BT-KNN ceramics by Zhang *et al.* (2007), which showed a pinched P - E loop and sprout-shaped strain curve, with a large maximum strain S_{max} of 0.45%, low remnant strain S_{rem} , and negative strain S_{neg} . Gao *et al.* (2011) firstly obtained the high energy storage density in BNT-based materials utilizing its dielectric relaxation behavior with slim P - E loop.

It is widely accepted that with the decrease of temperature down to approximately 520°C , the cubic phase of BNT transform to another paraelectric phase with a tetragonal symmetry P4bm , which showing an in-phase $a^0a^0c^+$ octahedral tilting combined with anti-parallel displacement of the $\text{Na}^+/\text{Bi}^{3+}$ and Ti^{4+} cations along $[001]_{\text{PC}}$. The phase in the temperature range of $200\text{--}320^\circ\text{C}$ is a topic of debate. Dorcet *et al.* (2008) suggested the existence of an orthorhombic intermediate phase with a Pnma space group and $a^-b^+a^-$ octahedral tilting based on the observations of $1/2\{\text{oe}\}$ superlattice reflections in the temperature range of $280\text{--}320^\circ\text{C}$, and the intermediate phase in the range of $200\text{--}280^\circ\text{C}$ is considered due to a reorientation of the polar moments with decrease of temperature, which means the phase transition from Pnma to low-temperature ferroelectric phase. Finally, the further decreasing temperature that frozen the polar region down to 200°C , emerging the ferroelectric R3c phase with the long-range ferroelectric order, which is also considered as the ground state of BNT, as shown in Fig. 10.

Piezoelectricity

For most of normal piezoelectric materials, the electric field induced strain and the force induced charge should be equal in value under a small applied external excitation. However, the electric field induced strain of BNT is quite unique. Therefore, in this section, the force-induced piezoelectric behavior is focused.

Due to the high electrical conductivity and large E_C , the poling of pure BNT materials is rather difficult, resulting in a low $d_{33} \sim 80$ pC/N. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3$ (BNT-BT) binary system is reported to have an enhanced piezoelectricity, where the MPB region for $(1-x)\text{BNT}-x\text{BT}$ was indicated to be located at $0.06 < x < 0.075$. A high $d_{33} \sim 186$ pC/N can be obtained, but

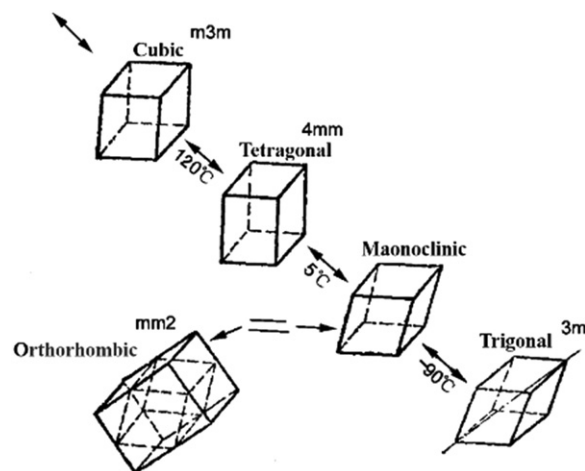


Fig. 8 The relationship between temperature and cell structure of BaTiO_3 .

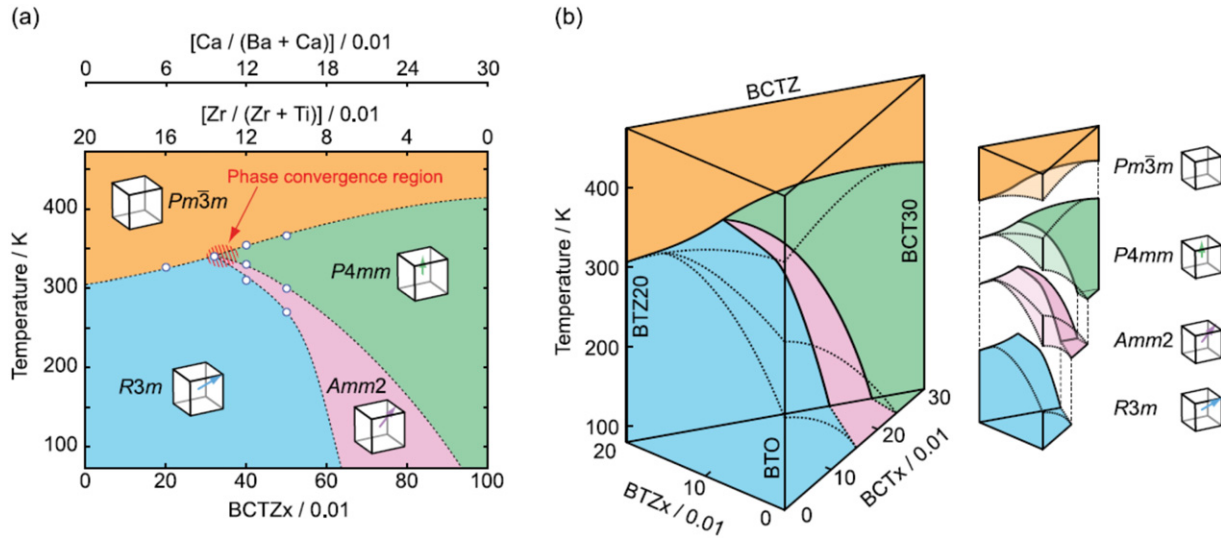


Fig. 9 (a) Suggested phase diagram of BZT-BCT based on the results from high-resolution synchrotron X-ray powder diffraction. (b) 3D phase diagram of BCTZ, showing how the two binary BTZ and BCT phases combine to form the ternary BCTZ, including an exploded view emphasizing the connectivity of the phases. Reproduced from Keeble, D.S., Benabdallah, F., Thomas, P.A., Maglione, M., Kreisel, J. 2013. Revised structural phase diagram of $(\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3)\text{-(BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3)$. Applied Physics Letter 102, 092903, with the permission of AIP Publishing.

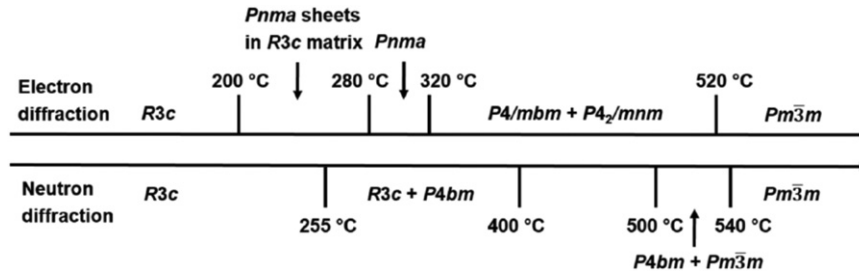


Fig. 10 Reported possible phase transition routes of BNT based on TEM and X-ray/neutron diffraction studies. Reproduced from Reichmann, K., Feteira, A., Li, M., 2015. Bismuth sodium titanate based materials for piezoelectric actuators. Materials 8, 8467–8495.

accompanying by a decreased T_d of $\sim 100^\circ\text{C}$ (Anthoniappen *et al.*, 2014). The piezoelectric and ferroelectric properties of $[\text{Bi}_{0.5}(\text{Na}_{1-x-y}\text{K}_x\text{Li}_y)_{0.5}\text{TiO}_3]$ piezoelectric ceramics show excellent piezoelectric and ferroelectric properties, and the optimum properties measured are as follows: piezoelectric constant $d_{33} = 231 \text{ pC/N}$, $k_p = 41.0\%$ and $k_t = 50.5\%$, $P_r = 40.2 \text{ } \mu\text{C/cm}^2$, and $E_C = 2.47 \text{ kV/mm}$, respectively (Lin *et al.*, 2006).

Maurya *et al.* (2013) reported on the microstructure and electric properties of grain-oriented 0.93BNT-0.07BT ceramics textured by single-crystal BNT plates, and the optimized d_{33} of the textured sample could reach 322 pC/N , which was twice as large as the randomly-oriented ceramic ($d_{33} \sim 160 \text{ pC/N}$). Some compositions with their piezoelectric properties are listed in Table 4.

Many attempts were made to improve the thermal stability of BNT-based ceramics, such as ion doping, formation of new solid solutions, texturing, grain size control, quenching, which aims to enhance structural thermal stability of long-range-ordered ferroelectric state. Zhang *et al.* (2015a) reported that introduction of ZnO into BNT-BT to form a 0–3 type composite ceramic can result in the improvement or even disappearance of thermal depolarization without sacrificing the piezoelectric response.

Energy storage properties

In recent years, the ferroelectric/anti-ferroelectric dielectric energy storage applications have been paid much attention due to the potential high energy storage density (Yan *et al.*, 2020). From their typical P - E loop, recoverable energy density J_{reco} should be calculated via

$$J_{\text{reco}} = \int_{P_r}^{P_{\text{max}}} E dP \quad (3)$$

where the P_r and P_{max} are the remanent polarization and maximum polarization, respectively. In an AC period, the center area of P - E loop is equal to the loss of energy J_{loss} , which usually transfer to the thermal energy. To achieve the high energy storage density and high energy efficiency η [$\eta = J_{\text{reco}}/(J_{\text{reco}} + J_{\text{loss}})$], the low P_r and high P_{max} are goal for developing ferroelectric energy storage

applications. In the BNT-based ceramics, the “ER” state with numerous PNRs can be induced by compositional and microstructure design, which is by a slim P - E loop with high $P_{\max}$ under the external electric-field and low P_r on removal of the electric field. This characteristic is highly conducive to the good energy storage density, and some advances have achieved in BNT-based ceramics, as listed in Table 5.

(K,Na)NbO₃-based lead-free piezoceramics

Similar to PZT based piezoelectric ceramics, potassium sodium niobate ($K_xNa_{1-x}NbO_3$, KNN) ceramics are binary solid solutions formed by ferroelectric KNbO₃ and antiferroelectric NaNbO₃.

The piezoelectric constant d_{33} of pure KNN ceramics fabricated via solid state method is about 80 pC/N (Egerton and Dillon, 1959), which is rather small. Hence, some approaches have been utilized to enhance the electric properties of KNN ceramics, such as constructing phase boundaries, domain engineering and optimization of processing of preparing methods. Saito *et al.* (2004) reported the KNN-based textured ceramics presenting a peak d_{33} of 416 pC/N, piezoelectric coupling constant k_p of 0.61 and Curie temperature T_C of 253°C, which is comparable to performances of the conventional PZT-based ceramic (PZT4) for actuator applications. For further improvement of piezoelectric performances, researchers have carried out a series of studies on KNN based ceramics, such as constructing phase boundaries, domain engineering, and so on (Xu *et al.*, 2016; Li *et al.*, 2018b; Tao *et al.*, 2019).

Construction of phase boundaries near room temperature

Construction of phase boundaries near room temperature exerts a remarkable effect in increasing properties (Kutnjak *et al.*, 2006; Ahart *et al.*, 2008), which is in terms of compositional modifications in KNN-based ceramics (Wu *et al.*, 2015).

With the change of temperature, KNN ceramics undergo successive phase transitions from rhombohedral (R) to orthorhombic (O) at -123°C , orthorhombic to tetragonal (T) at $\sim 200^\circ\text{C}$ and tetragonal to cubic (C) transition at 410°C . The O-T phase transition temperature (T_{O-T}) can be tuned from $\sim 200^\circ\text{C}$ to near room temperature through doping compositions, such as Li(Sb/Ta)O₃ and Bi_{0.5}K_{0.5}/Bi_{0.5}Na_{0.5}/Ba/Ca/SrTiO₃. Then the phase structure of KNN-based ceramics changes from orthorhombic into the coexistence of orthorhombic and tetragonal phases to construct O-T phase boundary near room temperature, finally enhancing the piezoelectric properties. For example, the (K_{0.48}Na_{0.52})NbO₃-Bi_{0.5}Li_{0.5}ZrO₃ system was studied, which shows that the Bi_{0.5}Li_{0.5}ZrO₃-modified KNN ceramics changed a single phase structure with orthorhombic symmetry to O-T phase boundary near room temperature, presenting d_{33} value of 265 pC/N, k_p value of 0.365 and T_C of 364°C (Wu *et al.*, 2018a). The Bi_{0.5}Na_{0.5}HfO₃ was doped in (K_{0.48}Na_{0.52})NbO₃-0.004BiCoO₃ ceramics to change the phase structure from orthorhombic to tetragonal then constructing O-T phase boundary, finally enhancing the properties of d_{33} value of 272 pC/N, k_p of 0.47 and T_C of 333°C (Wen *et al.*, 2019).

Although the O-T phase boundary can improve the piezoelectric properties to some degree, their d_{33} values of KNN-based ceramics are often limited to be 200–300 pC/N, which is insufficient for replacing commercial lead-based ones for practical applications. The R-O phase transition temperature (T_{R-O}) and T_{O-T} of KNN-based ceramics can be tuned simultaneously to near

Table 4 Piezoelectric properties of BNT-based ceramics

Materials System	d_{33} (pC/N)	T_d ($^\circ\text{C}$)	k_p (%)	ϵ_r	$\tan\delta$ (%)	References
0.94BNT-0.06BT	186	100	56.4 (k_{33})	990	~ 8	Anthoniappen <i>et al.</i> (2014)
0.94BNT-0.06BT	155	105	36.7	826	2.5	Xu <i>et al.</i> (2008)
0.93BNT-0.07Ba(Ti _{0.945} Zr _{0.055})O ₃ + 0.25 mol% Mn	187	72	23	~ 1100	~ 3.5	Zhang <i>et al.</i> (2018b)
0.80BNT-0.20BKT	157	174	54 (k_{33})	884	~ 4	Yoshii <i>et al.</i> (2006)
0.80BNT-0.20BKT	195	100	27.03	1743	5.3	Moosavi <i>et al.</i> (2014)
0.70BNT-0.20BKT-0.10Bi _{0.5} Li _{0.5} TiO ₃	231	125	34	~ 1160	~ 4.7	Lin <i>et al.</i> (2008)
0.854BNT-0.026BT-0.12BKT	295	/	/	/	/	Shieh <i>et al.</i> (2007)
0.935BNT-0.065BT	361	/	/	/	/	Shieh <i>et al.</i> (2007)

Note: d_{33} -piezoelectric constant; T_d -depolarization temperature; k_p -electromechanical coupling factor; ϵ_r -dielectric constant; $\tan\delta$ -dielectric loss.

Table 5 The high electric-field-induced strain of BNT-based ceramics

Materials system	J_{reco} (J/cm ³)	η (%)	E (kV/mm)	Temperature stability ($^\circ\text{C}$)	References
0.60BNT-0.40Sr _{0.7} Bi _{0.2} TiO ₃	2.2	75	16	20–140	Qian <i>et al.</i> (2019)
0.80BNT-0.20NaTaO ₃	4.21	77.8	38	-50–300	Zhou <i>et al.</i> (2019)
0.78BNT-0.22NaNbO ₃	7.02	85	39	25–250	Qi and Zuo (2019)
0.90BNT-0.10LiTaO ₃	2.30	74.2	20	30–120	Zhang <i>et al.</i> (2020)
0.8BNT-0.2SrNb _{0.5} Al _{0.5} O ₃	6.64	96.5	52	30–150	Yan <i>et al.</i> (2020)

Note: J_{reco} -recoverable energy storage density; η -energy storage efficiency; E -applied electric field.

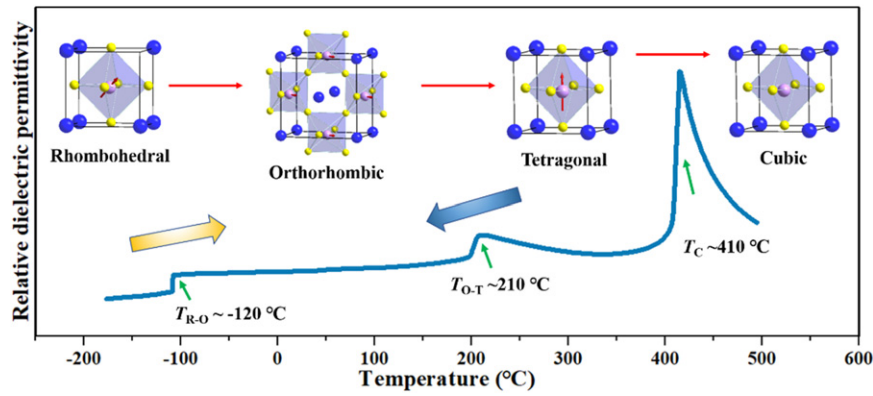


Fig. 11 The schematic diagram of phase transition structure and design idea of new phase boundary in KNN-based ceramics.

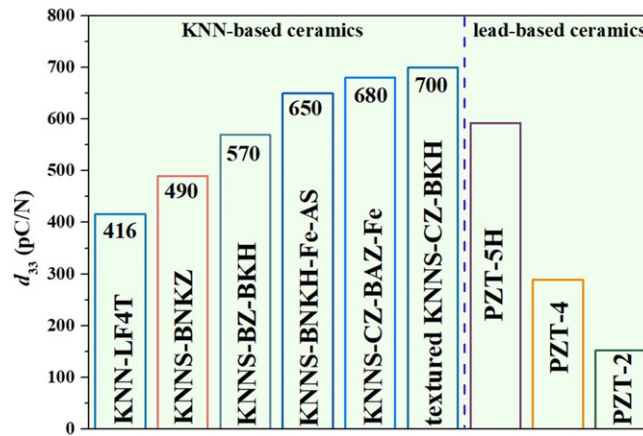


Fig. 12 Comparison diagram of piezoelectric properties of KNN-based ceramics and lead based ceramics.

room temperature by chemical modification, as shown in Fig. 11, constructing the phase boundaries (R-O-T and R-T) to realize high electrical properties comparable to that of PZT materials.

At the same time of decreasing T_{O-T} in KNN ceramics, doing ions (Sb^{5+} , Ta^{5+}) or compounds, such as $\text{Bi}_{0.5}(\text{K}/\text{Na}/\text{Li}/\text{Ag})_{0.5}(\text{Zr}/\text{Hf})\text{O}_3$, $(\text{Ba}/\text{Ca}/\text{Mg})\text{ZrO}_3$, $\text{Bi}(\text{Sc}/\text{Co}/\text{Fe})\text{O}_3$ can enhance the proportion of rhombohedral and tune the T_{R-O} from -123°C to near room temperature, then constructing the R-O-T or R-T phase boundaries.

The R-O-T phase boundaries can be constructed via tuning T_{O-T} and T_{R-O} , that is, there is a coexistence of R, O and T phases near room temperature. The construction of R-T phase boundaries is to compress the temperature range between T_{O-T} and T_{R-O} , then merging into one single dielectric peak and forming a new phase boundary, that is, there is a coexistence of R and T phases near room temperature. In the case of multi-phase coexistence, a lower energy barrier exists between phases, and nearly vanishing polarization anisotropy makes polarization rotation easily happen.

High d_{33} values of 490–570 pC/N were achieved via the constructing R-T phase boundaries (Wang *et al.*, 2014; Xu *et al.*, 2016; Tao *et al.*, 2019). It should be noted, high d_{33} value of 650 ± 20 pC/N can be obtained by introducing relaxor behavior in R-O-T phase boundaries (Tao *et al.*, 2019). Due to the relaxor properties and nanodomains, a high piezoelectric constant of 680 ± 10 pC/N was also obtained in KNN-based ceramics (Go *et al.*, 2021). In particular, an ultrahigh property with $d_{33} \sim 700$ pC/N and electromechanical coupling factor (k_p) $\sim 76\%$ were realized in highly textured KNN-based ceramics (Li *et al.*, 2018b). The performances of KNN based ceramics have so far been improved up to the level of some commercial PZT based ceramics, as indicated in Fig. 12.

Domain engineering

The domain is an area with the same spontaneous polarization direction and domain wall separates two domains (Lv *et al.*, 2020), which can be observed via transmission electron microscope (TEM), piezoresponse force microscopy (PFM) and chemical etching. The piezoelectric response of piezoelectrics is composed of intrinsic and extrinsic contributions. The intrinsic contribution is mainly related to the lattice distortion (Zheng *et al.*, 2018b) and the extrinsic ones are associated with domain switching and domain wall engineering. Hence, domain structure plays also an important role in enhancing electric performances in piezoelectric ceramics as extrinsic contribution.

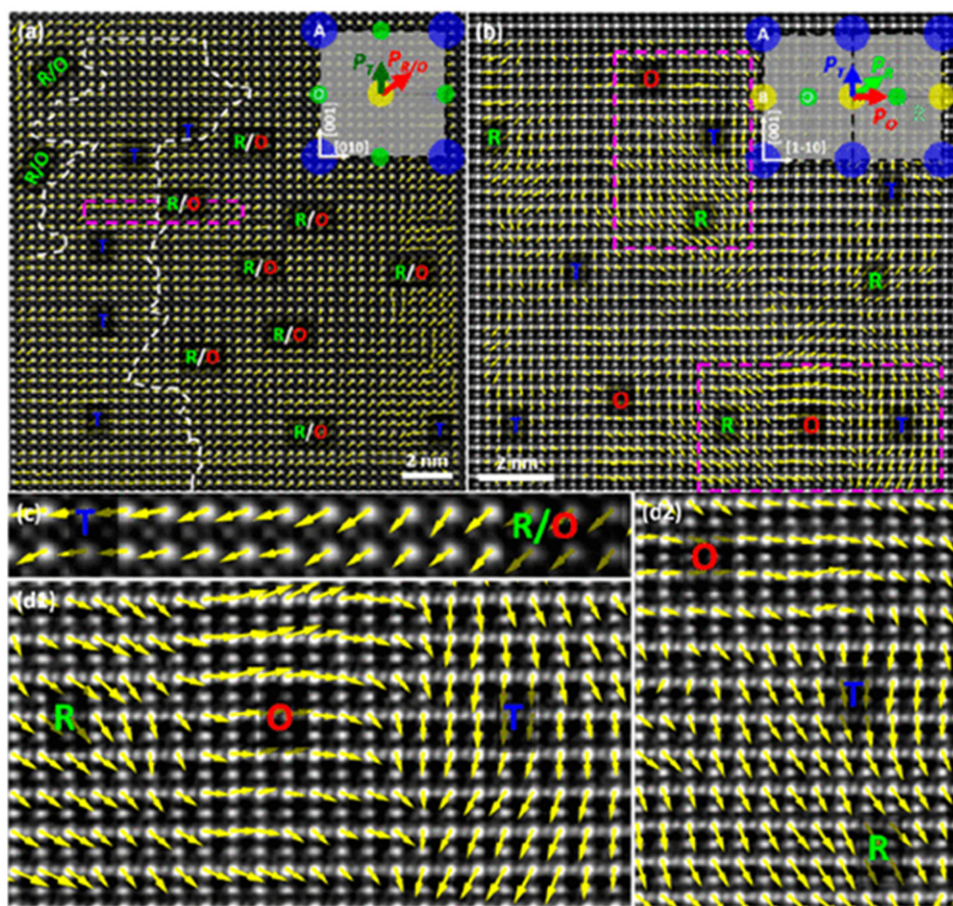


Fig. 13 Local symmetry and polarization mapping inside nanodomains. (a) Atomically resolved STEM HAADF image along [100], with the $\delta_{\text{Nb-Na}}/\kappa$ displacement vector map overlaid on it; the displacement vectors are indicated as arrows, and T and O/R regions are marked. (b) Atomically resolved contrast-reversed STEM ABF image along [110], with the $\delta_{\text{Nb-O}}$ displacement vector map overlaid on it; the displacement vectors are indicated as arrows, and T, O, and R regions are marked. (c) Enlarged image showing polarization rotation from T to O/R. (d₁, d₂). Enlarged images showing polarization rotation from R to O to T. Reproduced from Tao, H., Wu, H., Liu, Y., *et al.*, 2019. Ultrahigh performance in lead-free piezoceramics utilizing a relaxor slush polar state with multiphase coexistence. *Journal of the American Chemical Society* 141, 13987-13994, with the permission of AMERICAN CHEMICAL SOCIETY.

Domain size is closely related to the excellent piezoelectric properties of ceramics. Compared with the regular domain structures with micron-scale size of pure KNN ceramics, the KNN ceramics with O-T phase boundaries near room temperature show the irregular submicron island-shaped and lamellar domains. The KNN-based ceramics with R-O-T/R-T phase boundaries near room temperature can exhibit submicron or nanoscale domains, which can reduce domain wall energy and easily respond to external electric field, contributing to improving piezoelectric properties (Liu *et al.*, 2018).

The ultra-fine nanodomains with 4–5 nm in width and 7–27 nm in length can be observed in $(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.955}\text{Sb}_{0.045})\text{O}_3-0.01\text{SrZrO}_3-(\text{Bi}_{0.5}\text{Ag}_{0.5})\text{ZrO}_3$ ceramics with d_{33} values of 487 pC/N (Sun *et al.*, 2019). The polar domains with 2 nm size makes KNN-based ceramics present an ultrahigh d_{33} value of 650 ± 20 pC/N (Tao *et al.*, 2019), as shown Fig. 13. Hence, the domain engineering can be controlled to further enhance the piezoelectric properties of KNN-based ceramics.

BiFeO₃-based lead-free piezoceramics

Introduction of BiFeO₃ ceramics

BiFeO₃, as a ceramic with high T_C (825°C) and excellent piezoelectric properties at the same time, has recently emerged as a substitution to replace PZT. The Bi element is adjacent to Pb on the periodic table and has the same electron distribution, similar ionic radius and molecular weight. In extensive research on lead-based piezoelectric ceramics, it is believed that the 6s² lone pair of electrons of Pb is lead-based piezoelectric ceramics. Because Bi has similar lone pair electronic properties to lead and its oxide is non-toxic, Bi-based ferroelectric BiFeO₃ is naturally expected to be a potential lead-free piezoelectric ferroelectric material. The first-principles calculations show that BiFeO₃ has good piezoelectric properties. The theory predicts that the BiFeO₃ saturation polarization can reach at 100 $\mu\text{C}/\text{cm}^2$ at room temperature. It is currently a rare single-phase multiferroic material known to have both ferroelectricity and magnetism above room temperature (Choi *et al.*, 2009; Zeches *et al.*, 2009). BiFeO₃ crystal structure is

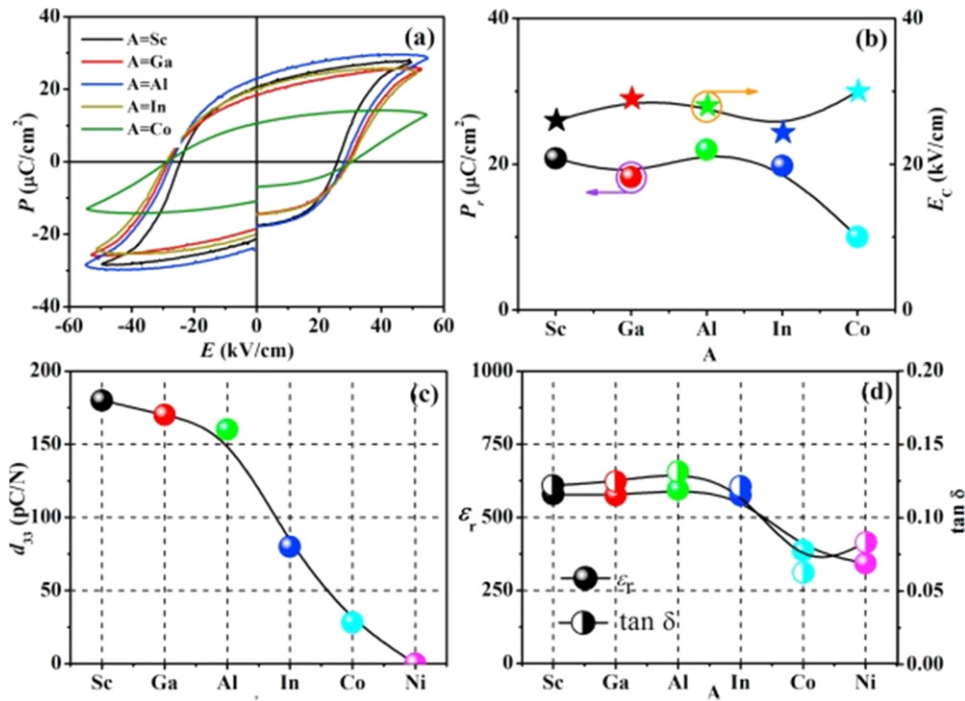


Fig. 14 (a) P - E loops, (b) P_r and E_c , (c) d_{33} , (d) ϵ_r and $\tan \delta$ of 0.7Bi_{1.05}Fe_{0.97}A_{0.03}O₃-0.3BaTiO₃ ceramics as a function of A elements. Reproduced from Zheng, T., Jiang, Z., Wu, J., 2016b. Enhanced piezoelectricity in (1-x)Bi_{1.05}Fe_{1-y}AyO₃-xBaTiO₃ lead-free ceramics: Site engineering and wide phase boundary region. Dalton Transactions 45 (28), 11277-11285, with the permission of Elsevier.

trigonal twisted rhombohedral perovskite structure, belonging to $R3c$ space group, lattice constant is $a = 5.55787 \text{ \AA}$, $c = 13.8688 \text{ \AA}$. The crystal orientation of the hexagonal structure $[001]_h$ is parallel to the $[111]_c$ crystal orientation in the rhombohedral perovskite structure.

Due to the narrow synthesis temperature window of BiFeO₃, the product is likely to be accompanied by the second phase, such as Bi₂Fe₄O₉, Bi₃₆Fe₂O₅₇, etc. During the sintering process, Fe³⁺ is easily converted to Fe²⁺ and a large number of oxygen vacancies are generated, which leads to large leakage conductivity and it is difficult to detect the saturation hysteresis loop. In order to improve the electrical properties of the material, it is currently modified by two methods, one is doping with elements, such as La, Tb, Mn, Ti, Dy, Sm doping; the other is with other ABO₃ type ferroelectrics such as BaTiO₃, SrTiO₃, CaTiO₃, NaNbO₃, K_{0.5}Na_{0.5}NbO₃, and Bi_{0.5}K_{0.5}TiO₃, form solid solutions to stabilize their perovskite structure. The introduction of ABO₃ can not only stabilize the perovskite structure of the base material, suppress the impurity phase, and increase the resistivity, but also construct MPB in the BF-ABO₃ solid solution.

The first time (1-x)BiFeO₃-xBaTiO₃ (BFBT) ceramics was synthesized through traditional solid-phase method by Fedulov *et al.* (1964), and then it was confirmed by Kumar *et al.* (2000). Leontsev and Eitel (2009) drew a revised phase diagram and showed that there are R and C phase MPB at 0.25-0.4BT, which possess excellent piezoelectric properties. Enhanced piezoelectricity ($d_{33} = 124$ -240 pC/N) can be observed in BFBT ceramics (Yang *et al.*, 2013; Zheng *et al.*, 2016a) due to the involvement of phase boundaries. Recently, ion substitutions (Nd, La, Ga, Al, Sc, Co, etc.) were employed to further modify the BFBT ceramics, which can partly enhance the piezoelectricity due to the presence of phase boundaries together with the improved microstructure. For instance, doping with Nd₂O₃ (Zheng *et al.*, 2014), Al₂O₃ (Cen *et al.*, 2013), La₂O₃ (Wu *et al.*, 2015) or Ga₂O₃ (Lee *et al.*, 2015) can induce phase transitions, and the improved electrical properties were mainly attributed to the formation of phase boundaries. Fig. 14 shows the electrical properties of 0.7Bi_{1.05}Fe_{0.97}A_{0.03}O₃-0.3BaTiO₃ (A = Sc, Ga, Al, In, Co, Ni) ceramics as a function of the A element. Saturated P - E loops and large piezoelectricity ($d_{33} = 160$ -180 pC/N) can be attained simultaneously in ceramics with Sc, Ga, and Al due to the presence of a R-Pc phase boundary (Zheng *et al.*, 2016b). In particular, in 2015, a large piezoelectricity was found in BiGaO₃-modified BFBT ceramics prepared by the conventional solid-state method together with quenching sintering, that is, a large d_{33} of 402 pC/N and a high T_C of 454°C were obtained simultaneously due to the formation of an R-T phase boundary (Lee *et al.*, 2015).

Another effective way to tailor the electrical properties of BFBT ceramics is to introduce a third component, such as Bi(Mg_{0.5}Zr_{0.5})O₃, Bi(Mg_{0.5}Ti_{0.5})O₃, Bi(Zn_{0.5}Ti_{0.5})O₃, Bi_{0.5}Na_{0.5}TiO₃, Bi_{0.5}K_{0.5}TiO₃, Bi(Ni_{0.5}Ti_{0.5})O₃ and so on. More interestingly, different phase boundaries can be constructed by optimizing the compositions of ABO₃. For example, a R-T phase boundary can be formed by doping Bi(Zn_{0.5}Ti_{0.5})O₃ (Lee *et al.*, 2015), Bi(Mg_{0.5}Zr_{0.5})O₃ (Luo *et al.*, 2014) or Bi_{0.5}Na_{0.5}TiO₃ (Li *et al.*, 2015) into the BFBT matrix, and the rhombohedral-pseudocubic (R-Pc) phase boundary has been reported in BF-BT-Bi_{0.5}K_{0.5}TiO₃ ceramics (Lin *et al.*, 2013). Sun *et al.* (2021) reported that (1-x)BiFeO₃-xBaTiO₃-Bi(Zn_{0.5}Ti_{0.5})O₃ + MnO₂ + Li₂CO₃ ceramics shown R-Pc phases coexist in the ceramic structure when $x = 0.3$. The d_{33} , T_C , and depolarization temperature T_d of the ceramics are as high as 184 pC/N, 550°C, 530°C at $x = 0.3$, respectively.

Table 6 Properties of some BFBT-based ceramics

Materials System	d_{33} (pC/N)	T_C (°C)	k_p (%)	$\tan\delta$ (%)	Reference
0.75BF-0.25BT-MnO ₂	116	619	—	4.6	Leontsev and Eitel (2009)
0.7BF-0.3BT-xCo ₂ O ₃	151	—	32	—	Huang <i>et al.</i> (2018)
0.71BF-0.29BT-xMnO ₂	169	500	37.3	4.4	Li <i>et al.</i> (2016)
0.70Bi _{1-y} (Fe _{0.96} Mg _{0.02} Ti _{0.02})O ₃ -0.30BaTiO ₃	198	497	30.9	6.1	Zhu <i>et al.</i> (2017)
BF-BT _x + MnO ₂ + CuO	170	485	34.2	—	Yang <i>et al.</i> (2013)
0.72BiFeO ₃ -0.28BaTi _{1-x} Nb _x O ₃	149	—	—	—	Zhou <i>et al.</i> (2015)
0.725BiFe _{1-x} Al _x O ₃ -0.275BaTiO ₃ -1mol% MnO ₂	138	—	32.7	—	Fan <i>et al.</i> (2015)
0.71BiFe _{1-x} (Zn _{0.5} Ti _{0.5}) _x O ₃ -0.29BaTiO ₃	165	380	32.1	—	Shan <i>et al.</i> (2013)
0.7Bi _{1-x} Ca _x FeO ₃ -0.3BaTiO ₃	168	420	28	—	Wang <i>et al.</i> (2018)
0.75(Bi _{1-x} La _x)FeO ₃ -0.25BaTiO ₃	168	410	33.5	—	Zhou <i>et al.</i> (2013)
0.67Bi _{1.05} Fe _{0.97} Ga _{0.03} O ₃ -0.33BaTiO ₃	402	454	—	—	Lee <i>et al.</i> (2015)

Note: d_{33} -piezoelectric constant; T_C - Curie temperature; k_p -electromechanical coupling factor; ϵ_r -dielectric constant; $\tan\delta$ -dielectric loss.

Difficulties in improving the performance of BFBT ceramics

BFBT ceramics have excellent piezoelectric and ferroelectric properties when the composition is located near MPB. However, due to the volatilization of Bi₂O₃ and the change of Fe³⁺ in the sintering process of BFBT ceramics, the defect ion concentration of the ceramic samples became higher, which in turn leads to higher leakage current, higher dielectric loss $\tan\delta$, and poor piezoelectric performance. In view of the above situation, the researchers solve the problem from the following aspects.

(1) Oxide doping

In BTBT ceramics, in order to solve the problems of the volatilization of Bi₂O₃ and the changing valence of Fe³⁺, it is often suppressed by using excessive amounts of Bi₂O₃ and adding oxides (such as Mn and Cu) to reduce its defect concentration. Oxide doping and performance are shown in Table 6.

(2) Ion substitution

Ion substitution is also considered to be an effective method to improve the piezoelectric properties of BF-BT ceramics. Ion substitution is divided into A-site ion substitution and B-site ion substitution. The A-site ion substitution elements mainly include rare earth ions such as La³⁺, Ca²⁺. B-site ion substitution can effectively reduce the content of Fe³⁺ ions, thereby reducing the price of Fe³⁺. The B-site ion substitution elements mainly include Nb⁵⁺, Al³⁺, and (Zn_{0.5}Ti_{0.5})³⁺, as shown in Table 6.

(3) Optimization of process

In the preparation process of BF-BT ceramics, high sintering temperature will cause the volatilization of Bi₂O₃. Although lowering the sintering temperature can slightly reduce the volatilization, it is not conducive to improving the compactness of the ceramic, so there are the following ways to optimize the process:

(1) Increase sintering time;

(2) Use water quenching after sintering;

The latter can effectively reduce Bi₂O₃ volatilization and reduce the pinning effect of defects on domain walls (Qin *et al.*, 2018). The recently progress of lead-free piezoelectric ceramics with perovskite structure is show as Fig. 15.

Tungsten Bronze Structure Based Lead -Free Piezoceramics

Non-filled tungsten bronze structure

A typical ferroelectric material with non-filled tungsten bronze structure is Sr_{1-x}Ba_xNb₂O₆ (SBN), which has excellent piezoelectric properties and electro-optical properties, has application prospects in the fields of nonlinear optics, piezoelectric and surface acoustic wave sensor devices (Ewbank *et al.*, 1987). It is a solid solution formed by the binary system of SrNb₂O₆ and BaNb₂O₆. It has a certain solid solubility limit, which is generally considered to be $x = 0.25-0.75$. With the change of Sr and Ca content, the T_C of the material changes, and the transition from normal ferroelectric to dispersed phase transition to relaxation ferroelectric occurs. The materials with specific microstructure, ferroelectric and dielectric properties can be obtained by changing the composition (Jamieson *et al.*, 1968). SBN has a high pyroelectric coefficient (Glass, 1969) and effective electro-optical coefficient (Ewbank *et al.*, 1987). For example, the electro-optic coefficient of (Sr_{0.61}Ba_{0.39})Nb₂O₆ polarized single crystal in a non-clamped free state is $r_{13} = 47 \pm 5$ pm/V, $r_{33} = 235 \pm 21$ pm/V, higher than many other commonly used electro-optical materials (Ducharme *et al.*, 1987). The pyroelectric coefficient of (Sr_{0.75}Ba_{0.25})Nb₂O₆ single crystal is as high as $0.31 \mu\text{C}/(\text{cm}^2 \text{ K})$, which is much higher than other pyroelectric materials with perovskite structure (Glass, 1968).

Filled tungsten bronze structure

The filled tungsten bronze is the most extensive in the research of tungsten bronze structure and has many different types. Its general structural formula can be expressed as A₆B₁₀O₃₀. The ions occupying the A site are usually alkali metal, alkaline earth metal or mellow metal element ions, and the ions occupying the B site are generally Nb⁵⁺ and Ta⁵⁺, but trivalent, tetravalent or

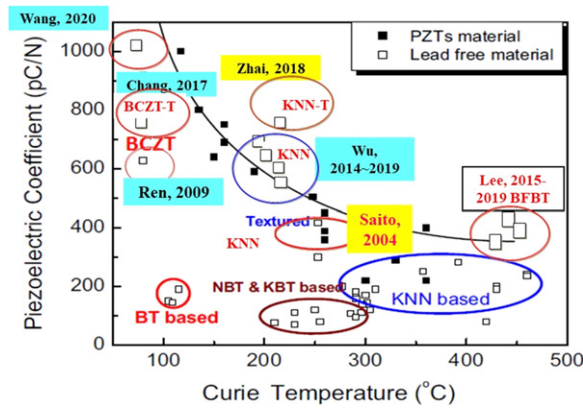


Fig. 15 Recently progress of lead-free piezoelectric ceramics with perovskite structure.

hexavalent Ti^{4+} , Zr^{4+} , W^{6+} and Fe^{3+} plasmas can also be introduced to maintain the overall electricity price balance of the compound and regulate the material properties at the same time (Hwang and Kwon, 1997; Chi *et al.*, 2004). The piezoelectric and ferroelectric properties of $\text{Sr}_{2-x}\text{Ca}_x\text{NaNb}_5\text{O}_{15} + \gamma \text{ wt\% MnO}_2$ ceramics show excellent piezoelectric and ferroelectric properties. For the ceramic with $x = 0.05$ and $\gamma = 0.5$, the optimum properties measured are as follows: $d_{33} = 190 \text{ pC/N}$, $k_p = 13.4\%$, $k_t = 36.5\%$, $\epsilon_r = 2123$, $\tan \delta = 0.038$, $P_r = 4.76 \mu\text{C/cm}^2$, $E_c = 12.68 \text{ kV/cm}$, and $T_c = 260^\circ\text{C}$, respectively (Fan *et al.*, 2011).

Since the full-filled tungsten bronze has strong tunability and rich dielectric and ferroelectric phase change characteristics, more and more related researches are concentrated in this field.

Fully filled tungsten bronze structure

$\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ is a typical full-filled tungsten bronze material, which has good nonlinear optical characteristics and resistance to light damage (Neurgaonkar *et al.*, 1989). The growth of $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ single crystals using the Czochralski method has a strong longitudinal effect and can be used in the fields of surface acoustic wave sensors, electro-optical and photorefractive devices (Neurgaonkar *et al.*, 1989), but the crystals are prone to cracking during the growth process. Recent studies have shown that when MgO is incorporated into the crystal, the linear expansion coefficient of the crystal will drop very significantly, which can effectively solve this problem. In addition, the crystal has a large electromechanical coupling coefficient, and it can remain basically unchanged from room temperature to 250°C (Cheng *et al.*, 2000). Table 7 compares the properties of different piezoelectric materials.

Bismuth Layered Structure Lead-Free Piezoceramics

$(\text{Bi}_2\text{O}_2)^{2+} + (\text{AB}_2\text{O}_7)^{2-} (m=2)$ based ceramics

$(\text{Bi}_2\text{O}_2)^{2+} + (\text{AB}_2\text{O}_7)^{2-}$ based ceramics mainly includes $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBN), $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ (NBN) and other systems with high T_c ($>700^\circ\text{C}$), and is expected to be used in high temperature piezoelectric sensor. The T_c of CBN (943°C) is the highest in the BLSFs family (Long *et al.*, 2013). Researchers have carried out a lot of research on how to improve the piezoelectric activity, and some achievements have been achieved by chemical doping as shown in Table 8. Through introducing Bi and Mn ion, the d_{33} of CBN-based ceramic increases up to 20.8 pC/N that is nearly three times larger than that of pure CBN ceramic, and maintains high T_c (953°C). Except for single ion, compound ions are used to replace A-site and B-site of CBN-based ceramics together such as (LiNd, WSc) and (LiNd, WMn), and so on, and can realize the huge improvement of piezoelectric properties. Single ion or metal oxide is introduced into NBN-based ceramics, and it can be seen that increasing d_{33} and decreasing T_c is obtained after doping.

$(\text{Bi}_2\text{O}_2)^{2+} + (\text{A}_2\text{B}_3\text{O}_{10})^{2-} (m=3)$ based ceramics

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) ceramics is one of the earliest Bismuth layered ceramics studied by scientists, which belongs to $(\text{Bi}_2\text{O}_2)^{2+} + (\text{A}_2\text{B}_3\text{O}_{10})^{2-}$ ($m=3$) based ceramics. It is found that the density and electrical properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ can be improved by doping. Rare earth elements (La, Sm, Nd, Dy, Ce) can replace the A-position element Bi in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics, while the high-valued ions (Nb, Ta, W, V) can replace the B-position element Ti. However only a few researchers have raised the d_{33} of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ above 30 pC/N . As exhibited in Table 8, doping can effectively improve the properties of BiT. Xie *et al.* (2019) prepared piezoelectric ceramics with excellent performance by co-doping $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics with Mg and Nb elements, and the d_{33} and P_r of the best components reached 30 pC/N and $15.5 \mu\text{C/cm}^2$, respectively. By co-doping CuNb the BiT-based ceramic reaches highest d_{33} (38 pC/N).

$(\text{Bi}_2\text{O}_2)^{2+} + (\text{A}_3\text{B}_4\text{O}_{13})^{2-} (m=4)$ based ceramics

Compared with other bismuth layered ceramics, $(\text{Bi}_2\text{O}_2)^{2+} + (\text{A}_3\text{B}_4\text{O}_{13})^{2-}$ -based piezoceramics have excellent iron-voltage and electric properties, moderate T_c and low sintering temperature. The materials most studied in recent years include $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics, $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ceramics, and $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ ceramics.

Table 7 Comparing the properties of different piezoelectric ceramics

Materials system	d_{33} (pC/N)	T_C (°C)	k_p (%)	ϵ_r	Q_m	$\tan\delta$ (%)	References
BaTiO ₃	190	115	0.36	1700	300	0.1	Uchino (2000)
PZT-5A	374	365	0.6	1700	75	0.02	Hooker (1998)
PZT-5H	593	193	0.65	3400	65	0.02	Hooker (1998)
0.36BS-0.64PT	450	460	0.56	2010	–	–	Eitel <i>et al.</i> (2002)
(K _{0.44} Na _{0.52} Li _{0.04})(Nb _{0.84} Ta _{0.10} Sb _{0.06})O ₃	416	253	0.61	1570	–	–	Saito <i>et al.</i> (2004)
Pb ₂ Nb ₂ O ₆	85	570	0.36	225	11	–	Jaffe (1958)
Sr _{0.53} Ba _{0.47} Nb ₂ O ₆	–	77	–	2774	–	–	Podlozhenov <i>et al.</i> (2006)
K ₃ Li ₂ Nb ₅ O ₁₅	52	401	0.46	115	–	–	Neurgaonkar <i>et al.</i> (1989)

Table 8 Properties of some BLSFs

Systems	T_C (°C)	d_{33} (pC/N)	References
CBN-Bi-Mn	953	20.8	Long <i>et al.</i> (2020a)
CBN-LiNd-WSc	908	20.6	Long <i>et al.</i> (2013)
CBN-LiNd-WMn	946	21.1	Long <i>et al.</i> (2020b)
NBN-LiCe-W	771	26.1	Sun <i>et al.</i> (2015)
NBN-LiNbO ₃ -CeO ₂	782	28	Wang <i>et al.</i> (2012)
NBN-Mn	643	25	Wang <i>et al.</i> (2012)
NBN-Nd	>600	24	Wang <i>et al.</i> (2015)
BiT-WCr	638	28	Chen <i>et al.</i> (2017)
BiT-MnNb	659	32.1	Xie <i>et al.</i> (2021)
BiT-CuNb	678	38	Li <i>et al.</i> (2019b)
BiT-WNb	665	32	Xie <i>et al.</i> (2019)
BiT-CuTa	677	34	Li <i>et al.</i> (2019a)

Note: d_{33} -piezoelectric constant; T_C - Curie temperature.

CaBi₄Ti₄O₁₅

The T_C of CaBi₄Ti₄O₁₅ (CBT) is higher, but its d_{33} is only about 4 pC/N. In order to overcome the shortcoming of low d_{33} , researchers have carried out many experimental studies on the modification of CaBi₄Ti₄O₁₅ ceramics. The d_{33} of CBT ceramics was increased to 23 pC/N through Nb/Mn co-doping by Shen *et al.* (2015), and the Curie temperature of CBT ceramics maintains about 790°C.

SrBi₄Ti₄O₁₅

The SrBi₄Ti₄O₁₅ (SBT) is a typical BLSF ceramics with T_C equal to 550°C, and it is an orthogonal phase structure below Curie temperature, and the lattice constants a , b and c are 5.4507 Å, 5.4376 Å and 40.9041 Å, respectively (Hervoches *et al.*, 2002). At present, the research on SBT ceramics mainly focuses on improving the preparation process, A/B doping and multiple recombination. For example, the electrical properties of SrBi₄Ti₄O₁₅ ceramics prepared by molten salt method are gradually improved with the increase of synthesis temperature and molten salt content within a certain range.

Na_{0.5}Bi_{4.5}Ti₄O₁₅

The T_C of Na_{0.5}Bi_{4.5}Ti₄O₁₅ (NBT) is 655°C, and belongs to $A2_1am$ crystal system. The lattice constants a , b and c are 5.427 Å, 5.460 Å and 40.65 Å, respectively. Yao *et al.* (2015) and Jiang *et al.* (2015) used two rare earth elements (LaCe) and (CeNd) to replace Bi, respectively, also succeeded in enhancing d_{33} more than 20 pC/N of NBT.

Perovskite-Like Structure Based Lead -Free Piezoceramics

Up to now, there are 7 kinds of PLS compounds with ferroelectricity (Yan *et al.*, 2009) that have been discovered, namely Ca₂Nb₂O₇, Sr₂Nb₂O₇, Sr₂Ta₂O₇, Ce₂Ti₂O₇, Pr₂Ti₂O₇, Nd₂Ti₂O₇ and La₂Ti₂O₇.

Ca₂Nb₂O₇

Ca₂Nb₂O₇ is colorless transparent crystal with T_C up to 1525°C (Ning *et al.*, 2010). It has monoclinic crystal symmetry and its space group is $P2_1$. Its lattice constant is (a , b , c) = (7.7000 Å, 13.3600 Å, 5.5000 Å) and (α , β , γ) = (90°, 90°, 98.4°), or similar (a , b , c , γ) = (7.80 Å, 13.39 Å, 5.50 Å, 98.34°). Ca₂Nb₂O₇ is composed of flat plates of perovskite structure, and the layered structure is stacked along the [010] direction.

Compared with ideal perovskite, the layered structure of Ca₂Nb₂O₇ has the following distortion:

- (1) By displacing oxygen ions to form a framework that almost preserves the shape of the oxygen octahedral, the adjacent oxygen octahedral rotate along the a -axis, forming a small rotation angle between each other;
- (2) In different oxygen octahedral, Nb ions have a shift away from the center of symmetry;
- (3) The Ca ions slightly shifted along the c -axis;
- (4) The Ca ions in the interlayer have a large shift along the b -axis, so it can be considered that the interlaminar Ca ions and the oxygen ions are in the same ac plane (Brandon and Megaw, 2006).

$\text{Sr}_2\text{Nb}_2\text{O}_7$

$\text{Sr}_2\text{Nb}_2\text{O}_7$ single crystal is colorless and transparent with a density of 5.17 g/cm^3 . It has strong piezoelectric and electro-optical effects at room temperature. $\text{Sr}_2\text{Nb}_2\text{O}_7$ is a layered perovskite structure stacked along $[010]$, containing corner-shared NbO_6 octahedra and 12-coordinated Sr cations, all of which are on mirror surface $x = 0$ and $x = 0.5$, with two non-equivalent A sites (Ishizawa *et al.*, 1975). $\text{Sr}_2\text{Nb}_2\text{O}_7$ is ferroelectric below 156°C and has spontaneous polarization (P_s) in the bc plane. P_s rotates to c -axis at 215°C and becomes paramagnetic at 1342°C . $\text{Sr}_2\text{Nb}_2\text{O}_7$ is orthonormal phase at room temperature (Ning *et al.*, 2013), the space group is $\text{Cmc}2_1$, and the lattice constants are $(a, b, c) = (3.9550 \text{ \AA}, 26.7800 \text{ \AA}, 5.7010 \text{ \AA})$. $\text{Sr}_2\text{Nb}_2\text{O}_7$ obtained by the spark plasma sintering (SPS) method has a Curie temperature $T_c = 1327 \text{ }^\circ\text{C}$ with a piezoelectric constant $d_{33} = 2.8 \pm 0.2 \text{ pC/N}$ (Ishizawa *et al.*, 1976), and ferroelectric spontaneous polarization along the c -axis. The resistivity of $\text{Sr}_2\text{Nb}_2\text{O}_7$ is greater than $1 \text{ M}\Omega \cdot \text{cm}$ in two directions at 600°C , which makes it a promising material for high temperature applications.

$\text{Sr}_2\text{Ta}_2\text{O}_7$

$\text{Sr}_2\text{Ta}_2\text{O}_7$ is an orthogonal phase at room temperature, the space group is Cmcm , and the lattice parameters are $a = 3.937 \text{ \AA}$, $b = 27.198 \text{ \AA}$, and $c = 5.692 \text{ \AA}$. $\text{Sr}_2\text{Ta}_2\text{O}_7$ and $\text{Sr}_2\text{Nb}_2\text{O}_7$ are isomorphic allotrope, layered perovskite structure stacked along the $[010]$ direction (Ishizawa *et al.*, 1976). All ions of $\text{Sr}_2\text{Ta}_2\text{O}_7$ are on the mirror surface $x = 0$ and $x = 0.5$, which is the same arrangement as $\text{Sr}_2\text{Nb}_2\text{O}_7$. $\text{Sr}_2\text{Ta}_2\text{O}_7$ has a very low ferroelectric phase transition temperature. When the temperature is lower than -107°C , it is an orthogonal ferroelectric phase, the space group is $\text{Cmc}2_1$, and the lattice parameters are $(a, b, c, \beta) = (3.94 \text{ \AA}, 27.2 \text{ \AA}, 5.69 \text{ \AA}, 90^\circ)$. When the temperature is higher than -107°C , it transforms into a paraelectric orthonormal phase (Cmcm).

$\text{Ce}_2\text{Ti}_2\text{O}_7$

The color of $\text{Ce}_2\text{Ti}_2\text{O}_7$ single crystal is black red and its melting point is 1700°C (Zakharov *et al.*, 1980). It is difficult to prepare $\text{Ce}_2\text{Ti}_2\text{O}_7$ at high temperature, because when the temperature is higher than 400°C , Ce (III) compounds tend to form thermodynamically stable Ce (IV), and Ce (III) compounds are unstable in the air. $\text{Ce}_2\text{Ti}_2\text{O}_7$ can be prepared under the atmosphere of inert gas Ar or reducing gas H_2 with lattice parameters of $(a, b, c, \gamma) = (7.74 \text{ \AA}, 12.99 \text{ \AA}, 5.5 \text{ \AA}, 98.6^\circ)$. $\text{Ce}_2\text{Ti}_2\text{O}_7$ sintered by SPS method at 4 GPa under high pressure in argon atmosphere is a typical PLS, and its space group is $P2_1$ at room temperature. According to the analysis of octahedral tilt and Ti^{4+} ions displacement, the ferroelectric spontaneous polarization of $\text{Ce}_2\text{Ti}_2\text{O}_7$ is along the c -axis. $\text{Ce}_2\text{Ti}_2\text{O}_7$ has only 180° ferroelectric domains. There are some phase transitions in $\text{Ce}_2\text{Ti}_2\text{O}_7$ at 1073°C , which may be its Curie point., The d_{33} of $\text{Ce}_2\text{Ti}_2\text{O}_7$ is $0.4 \pm 0.2 \text{ pC/N}$ after polarization, which confirms the ferroelectricity of $\text{Ce}_2\text{Ti}_2\text{O}_7$ (Gao *et al.*, 2015a).

$\text{Pr}_2\text{Ti}_2\text{O}_7$

$\text{Pr}_2\text{Ti}_2\text{O}_7$ single crystal is green and its melting point is 1600°C (Zakharov *et al.*, 1980). $\text{Pr}_2\text{Ti}_2\text{O}_7$ is monoclinic phase at room temperature (Sun *et al.*, 2013), space group is $P2_1$, lattice constants are $(a, b, c) = (7.704 \text{ \AA}, 12.996 \text{ \AA}, 5.485 \text{ \AA})$, $(\alpha, \beta, \gamma) = (90^\circ, 90^\circ, 98.51^\circ)$. The piezoelectric constants of the oriented $\text{Pr}_2\text{Ti}_2\text{O}_7$ ceramic prepared by the SPS method along the vertical and parallel to the pressure direction are $0.5 \pm 0.1 \text{ pC/N}$ and $0 \pm 0.1 \text{ pC/N}$, respectively, and its resistivity at 600°C is about $10^6 \Omega \text{ cm}$ (Gao *et al.*, 2013a).

$\text{Nd}_2\text{Ti}_2\text{O}_7$

There are reports that $\text{Nd}_2\text{Ti}_2\text{O}_7$ single crystal is transparent grass green, however, there are also reports that it is transparent purple red (Kimura *et al.*, 1974), with a melting point of 1800°C . $\text{Nd}_2\text{Ti}_2\text{O}_7$ is monoclinic ferroelectric phase at room temperature, space group is $P2_1$, lattice parameters are $(a, b, c, \gamma) = (7.704 \text{ \AA}, 12.996 \text{ \AA}, 5.485 \text{ \AA}, 98.51^\circ)$. Its spontaneous polarization is along the c -axis, $P_r \approx 9 \text{ } \mu\text{C/cm}^2$, $E_c = 200 \text{ kV/cm}$, ϵ_r is between 31 and 47, $d_{33} = 6.5 \text{ pC/N}$ (Bayart *et al.*, 2014). The crystal is corroded by boiling nitric acid after polarization, and it can be observed that the crystal is a single domain structure. The $\text{Nd}_2\text{Ti}_2\text{O}_7$ prepared by the self-propagation high-temperature synthesis (SHS) has a Curie temperature $T_c > 1560^\circ\text{C}$. The phase transition process from the ferroelectric phase to the paraelectric phase involves the rotation and tilt of the TiO_6 octahedra (Gao *et al.*, 2016).

$\text{La}_2\text{Ti}_2\text{O}_7$

The melting point of $\text{La}_2\text{Ti}_2\text{O}_7$ is 1790°C and the density is 5.79 g/cm^3 . Most researchers consider that $\text{La}_2\text{Ti}_2\text{O}_7$ is monoclinic phase at room temperature, space group is $P2_1$, and lattice parameters are $(a, b, c, \gamma) = (7.80 \text{ \AA}, 13.011 \text{ \AA}, 5.546 \text{ \AA}, 98.6^\circ)$ (Gasparin, 1975). The structure consists of corner-shared TiO_6 octahedral layers stacked along $[110]$. The connectivity of the octahedra is broken at the shear interface, and adjacent plates are shift from each other along the a -axis by half the thickness of TiO_6 octahedron (Tuyikeze *et al.*, 2020). $\text{La}_2\text{Ti}_2\text{O}_7$ single crystal has piezoelectric and electro-optical characteristics. The spontaneous polarization of the single crystal is along the c -axis and its $d_{33} = 16 \text{ pC/N}$ (Gao *et al.*, 2015b). $\text{La}_2\text{Ti}_2\text{O}_7$ single crystals are difficult to prepare and easy to split along the cleavage plane, so the research hotspot in recent years is $\text{La}_2\text{Ti}_2\text{O}_7$ -based ceramics. Pure $\text{La}_2\text{Ti}_2\text{O}_7$ ceramics have $d_{33} = 2.6 \text{ pC/N}$, $P_s \approx 5 \text{ } \mu\text{C/cm}^2$. However, its advantages are high Curie temperature ($T_c = 1458^\circ\text{C}$

$\sim 1481^\circ\text{C}$) and high resistivity (the resistivity is greater than $1\text{ M}\Omega\text{ cm}$ at 700°C), the overall electrical properties of $\text{La}_2\text{Ti}_2\text{O}_7$ ceramics can be significantly improved by doping. For example, when Ce is mixed into $\text{La}_2\text{Ti}_2\text{O}_7$ to form $\text{La}_{2-x}\text{Ce}_x\text{Ti}_2\text{O}_7$, the solubility of Ce is between 0.35 and 0.5. With the increase of Ce, lattice parameters $a/b/c$ decrease, Curie temperature decreases ($T_c = 1387^\circ\text{C} \sim 1440^\circ\text{C}$), dielectric constant and dielectric loss increase, and piezoelectric properties improve. The d_{33} of $\text{La}_{1.85}\text{Ce}_{0.15}\text{Ti}_2\text{O}_7$ ceramics prepared by SPS can reach $3.9 \pm 0.1\text{ pC/N}$ (Gao *et al.*, 2013b). The d_{33} of $\text{La}_2\text{Ti}_{1.96}\text{V}_{0.04}\text{O}_7$ ceramics prepared by conventional solid state sintering can reach $4.8 \pm 0.2\text{ pC/N}$ (Li *et al.*, 2020).

Applications

Up to now, some prototype devices such as resonator, transducers, transformers, and ultrasonic motors, and so on, were prepared using lead-free piezoelectric ceramics (Rödel *et al.*, 2015; Zheng *et al.*, 2018b; Thong *et al.*, 2019). The recent development of devices using lead-free piezoelectric ceramics was briefly described.

Energy harvesters

Byeon and Yoo (2014) investigated the electrical properties of $(\text{Na}_x\text{K}_{1-x})_{0.96}\text{Li}_{0.04}(\text{Nb}_{0.90}\text{Ta}_{0.10})_{0.998}\text{Zn}_{0.005}\text{O}_3$ ceramics, realizing an optimal $d_{33} \times g_{33}$ value of $10.47\text{ pm}^2/\text{N}$ ($x = 0.56$). A large $d_{33} \times g_{33}$ value of $11.59\text{ pm}^2/\text{N}$ was reported in Pr-doped BCTZ ceramics (Coondoo *et al.*, 2015).

An environment-friendly lead-free ultrasound-induced wireless energy harvester used $(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.95}\text{Sb}_{0.05})\text{O}_3\text{-(Bi}_{0.4}\text{La}_{0.1})(\text{Na}_{0.4}\text{Li}_{0.1})\text{ZrO}_3$ ceramics reaches a maximum output power of 45 mW/cm^2 (Jiang *et al.*, 2019). A high-output flexible ultrasound-based wireless energy harvesting device based on the synthesized KNNS-BNZ-0.004BFC ceramic is designed and manufactured, presenting an instantaneous power density of 52.07 mW/cm^2 from the incident ultrasound pressure of 1.90 MPa (Xing *et al.*, 2021).

Nanogenerators

The energy harvester including nanomaterials is often called nanogenerator (NG) (Wang and Song, 2006). A high output and cost-effective flexible nanogenerator was made by Jung *et al.* (2011). The device consists of a NaNbO_3 nanowire-poly(dimethylsiloxane) (PDMS) polymer composite and Au/Cr-coated polymer films. The NaNbO_3 nanowire-PDMS polymer composite device shows an output voltage of 3.2 V and output current of 72 nA (current density of 16 nA/cm^2) under a compressive strain of 0.23% .

Lin *et al.* (2012) fabricated a NG by making a composite of the nanotubes with BaTiO_3 nanotubes/polymer poly(dimethylsiloxane) (PDMS). The peak open-circuit voltage and short-circuit current of the NG reached a high level of 5.5 V and 350 nA (current density of 350 nA/cm^2), respectively. The BaTiO_3 nanotubes/PDMS composite is highly transparent and useful for a large-scale ($11 \times 11\text{ cm}$) fabrication of lead-free piezoelectric NG. It was used to directly drive a commercial liquid crystal display.

Sensors

Choy *et al.* (2006) fabricated the prototype piezoelectric accelerometers using a compressive type design, as shown in Fig. 16, with $0.90(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}0.05(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\text{-}0.05\text{BaTiO}_3$ (BNKBT-5) ceramic rings with dimensions of 12.7 mm outer diameter, 5.1 mm inner diameter and 2.3 mm thickness as transduction elements. The prototype accelerometer was calibrated by a back-to-back calibration method. The lead-free accelerometer has a mean sensitivity of 2.239 pC/ms^{-2} within 50 Hz to 10.1 kHz and the lead-based accelerometer has a mean sensitivity of 4.343 pC/ms^{-2} within 50 Hz to 8.24 kHz under $\pm 2.5\%$ sensitivity fluctuation limitation.

Yang *et al.* (2022) prepared $(1-x)\text{BiFeO}_3\text{-}x\text{BaTiO}_3\text{-}0.0035\text{MnO}_2\text{-}0.001\text{Li}_2\text{CO}_3$ (BF-xBT) ceramics were prepared by a solid state approach, and the d_{33} of BF-0.30BT ceramics was 184 pC/N . The sensitivity of BF-0.30BT piezoelectric accelerometer reaches the highest value of about 40 pC/g , and the sensitivity of BF-0.30BT piezoelectric accelerometer is quite stable from room temperature to 400°C .

Continuous piezoelectric $\text{BaTi}_{0.88}\text{Sn}_{0.12}\text{O}_3$ (BTS) films were deposited on the flexible glass fiber fabrics (GFF) by Yu *et al.* (2021). The self-powered sensors were made based on the ultra-thin, superflexible, and polarization-free BTS-GFF/PVDF composite piezoelectric films. In the low force region ($1\text{--}9\text{ N}$), the sensors have the outstanding performance with voltage sensitivity of 1.23 V/N and current sensitivity of 41.0 nA/N , respectively. The BTS-GFF/PVDF sensors can be used to detect the tiny forces of falling water drops, finger joint motion, tiny surface deformation, and fatigue driving with high sensitivity.

Actuators

It is commonly considered that an enhanced displacement of piezoelectric actuators can be realized by a multilayer ceramic actuator (MLCA). An MLCA using a LT-doped KNN ceramic as the active element was fabricated by Kim *et al.* (2009), and a displacement of $1\text{ }\mu\text{m}$ can be obtained under an input voltage of 150 V . Hussain *et al.* (2020) prepared 10-layers and 16-layers multilayers (MLs) of $0.942\text{KNN}50/50\text{--}0.58\text{BNZ}$ with Pt internal electrodes using wet method, which generate the effective d_{33} of 2500 and 3200 pC/N , respectively. Conversely, 10-layers MLAs can actuate with 2.21 mm of displacement at moderately lower applied voltage (480 V). The effective d_{33}^* of 10 and 16 layers were 4604 pm/V and 4118 pm/V , respectively.

Wang *et al.* (2006) prepared a higher fundamental resonance frequency (f_r) of 107.1 kHz , the fastest response time (FRT) of $9.3\text{ }\mu\text{s}$, and a comparable effective coupling coefficient (k_{eff}) of 0.15 can be obtained in the KNN-Li cymbal actuator. Lam *et al.* (2006) prepared a cymbal actuator using $0.90(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}0.05(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\text{-}0.05\text{BaTiO}_3$ ceramic as the driving element

with titanium endcaps. It was found that the f_r , FRT, k_{eff} and d_{33} of the actuator are 94.2 kHz, 9.3 μs , 0.15 and 1550 pC/N, respectively, which are comparable to those of the hard PZT cymbal actuator.

Ultrasonic transducers

An ultrasonic transducer with a center frequency of 5 MHz was manufactured based on the 1–3 KNS-BNZH/epoxy composite by Ke *et al.* (2019), with a broad bandwidth of 80% (–6 dB) and two-way insertion loss of –30 dB.

High-frequency ultrasound imaging transducers exhibiting a high center frequency of 24.5 MHz, a broad –6 dB bandwidth of 97% and a high-sensitivity are designed and fabricated by Xing *et al.* (2020) using KNN-BA-BNZ ceramics.

Textured lead-free $0.915(\text{K}_{0.45}\text{Na}_{0.5}\text{Li}_{0.05})\text{NbO}_3\text{--}0.075\text{BaZrO}_3\text{--}0.01(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (KNLN-BZ-BNT) piezoelectric ceramics prepared by Quan *et al.* (2021) using the tape-casting method and designed high-frequency ultrasonic transducer with center frequency higher than 80 MHz and a –6 dB fractional bandwidth of 52%.

Ultrasonic motors

Ultrasonic motor (USM) is a type of resonant actuator that can be widely used in mobile equipment, such as digital still cameras and cellular phones. A shear-mode ultrasonic motor, as shown in Fig. 16, using lead-free KNN-LN-Cu ceramics with a high Q_m as the driving element was developed by Li *et al.* (2008), and the highest revolution speed of 486 rpm was obtained at 34.5 kHz with the input voltage of approximately 180 V_{p-p} (peak to peak).

Fig. 16 (a) shows the structure of the shear mode motor using lead-free KNN-LN-Cu ceramics. The ceramic pieces were polarized along the radial direction: two of them are from the inner to outer direction and the other two are in the opposite direction as shown in Fig. 16(b). The shear strain can induce a bending mode (shear-shear mode) with a large driving force in a piezoelectric beam under resonance drive with a free boundary condition as shown in Fig. 16(c).

Miyake *et al.* (2020) developed a miniature ultrasonic motor using a BNT multilayered piezoelectric transducer. This multilayered structure was utilized to enhance the piezoelectric displacement and was equipped with elastic fins, which convert the

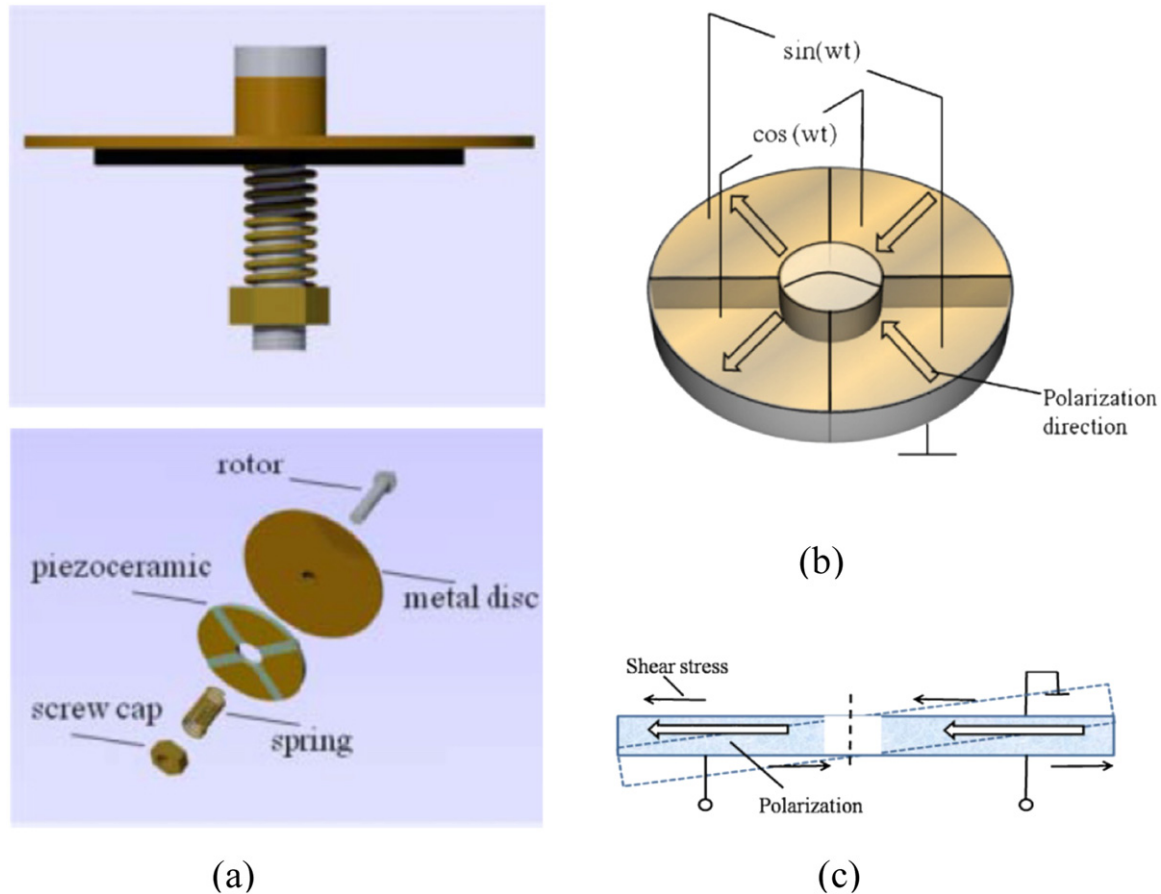


Fig. 16 (a) Structure of a rotary shear mode motor using KNN-LN-Cu piezoelectric ceramics; (b) Shape and polarization direction of the ceramic; (c) Sketch of bending mode excited by the shear-shear strain. Reproduced from Li, E., Kakemoto, H., Hoshina, T., Tsurumi, T., 2008. A shear-mode ultrasonic motor using potassium sodium niobate-based ceramics with high mechanical quality factor. Japanese Journal of Applied Physics 47 (9S), 7702–7706, with the permission of The Japan Society of Applied Physics.

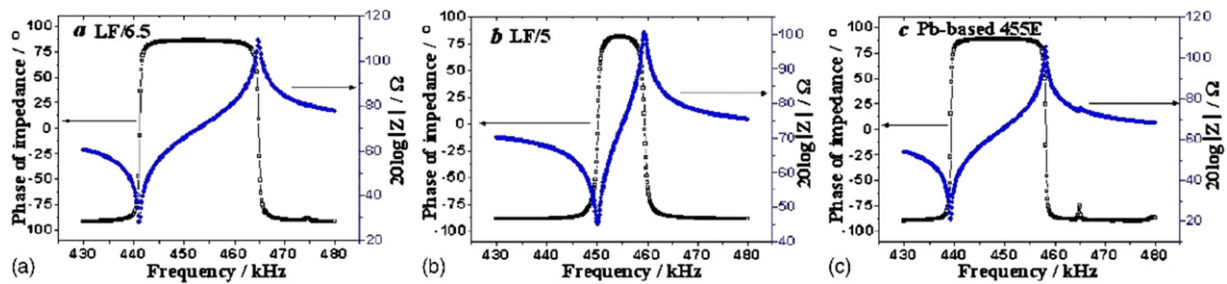


Fig. 17 Resonant characteristics of mid-frequency resonators of (a) LF/6.5, (b) LF/5, and (c) lead-based (455E). Reproduced from Chen, Q., Chen, L., Li, Q., et al., 2007. Piezoelectric properties of $K_4CuNb_8O_{23}$ modified $(Na_{0.5}K_{0.5})NbO_3$ lead-free piezoceramics. *Journal of Applied Physics* 102 (10), 104109., with the permission of AIP Publishing.

longitudinal vibration of the multilayered piezoelectric transducer into the rotational moment of the rotor. The rotational speed reached 922 rpm at a preload of 3 N under an input voltage of 58 V_{pp} and a resonance frequency of 60.0 kHz.

Resonators

Dense $K_4CuNb_8O_{23}$ modified $(K_{0.5}Na_{0.5})NbO_3$ (KNN:KCN) ceramics were synthesized by Chen *et al.* (2007). The Q_m , d_{33} and k_p of KNN:KCN ceramics reaches up to 1150, 100 pC/N and 40%, respectively. Two kinds of middle frequency (455 kHz) lead-free resonators, named LF/5 and LF/6.5, were fabricated by using KNN:KCN ceramics. The sizes of LF/6.5, LF/5 and lead-based 455 kHz resonator are 6.5 mm × 6.5 mm × 0.2 mm, 5 mm × 5 mm × 0.2 mm and 5 mm × 5 mm × 0.2 mm, respectively.

The phase-shift and resonance characteristics of lead-free NKN:xKCN 455 kHz resonator (LF/6.5), as shown in Fig. 17(a), are very similar to those of commercialized lead-based 455 kHz resonator, as shown in Fig. 17(c). However, the phase shift and resonance characteristics of LF/5 resonator degraded, as shown in Fig. 17(b). Both of the above mentioned lead-free resonator prototype devices can normally work at 2–6 V DC.

Electroacoustic transducers

An electroacoustic transducer is a device that converts an electric signal into an acoustic signal, which can be applied in smart mobile phones, laptops, and so on. Wu *et al.* (2008) prepared the buzzers using $(K_{0.5-x}Li_x)Na_{0.5}(Nb_{1-y}Sb_y)O_3$ ($x = 2.5$ mol% and $y = 5$ mol%, KLNNS2.5-5) ceramic membranes with diameters of 15–16 mm and thicknesses of 0.10–0.11 mm obtained by the roll forming process. It was found that the sound pressure level (SPL) reaches 84.2 dB at 2 kHz, which is slightly lower than that (SPL ≥ 85 dB) of the lead-based buzzers. In addition, a maximum value (~88.8 dB) of SPL was obtained at 2.81 kHz. The results show that the lead-free buzzers have good electroacoustic properties which can basically satisfy the requirements of practical applications, e.g., microwave ovens.

Gao *et al.* (2014) fabricated a flat panel micro speaker from three layers of 30-μm-thick KNN-based ceramics by a tape casting and cofiring process, as shown in Fig. 18. Fig. 19 shows the SPL and total harmonic distortion (THD) curves of the sample under different test voltages, compared with a PZT sample under 1 V_{rms}. The 23 × 27 × 0.6 mm³ micro speaker with three layers of 30 μm thickness KNN-based ceramics has the optimized acoustic properties: an average SPL of 87 dB and maximum SPL above 100 dB under 5 V_{rms} in the frequency range of 100 Hz to 20 kHz. The acoustic response of this lead free piezoelectric micro speaker under 1 V_{rms} is better than that of the PZT-based one.

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Photocatalysis

In order to relieve the problems of serious environment pollution and energy shortage, photocatalysis, including ferroelectrics, has been widely used in treating pollutants, water splitting and converting CO₂ to chemical fuels.

Pollution degradation Zhang *et al.* (2018a) reported the preparation of highly crystalline BaTiO₃ fibers by annealing treatment under 700, 800 and 900 °C (BT-700, BT-800 and BT-900), on which the BT-800 showed the highest photodegradation performance owing to the excellent ferroelectric properties and single-domain structure. Yin *et al.* (2020) found that ferroelectric external screening effect can promote the adsorption of dye molecules on the surface. The positive (negative) dipole accumulated surface will adsorb negatively (positively) charged dye molecules, which promoted degradation of dye molecules.

Water splitting Zhang *et al.* (2018c) prepared (001)-facet-exposed planelike ABi₂Nb₂O₉ (A = Ca, Sr, Ba) powders by the molten salt method. It was found that the H₂ and O₂ evolution activities of the planelike ABi₂Nb₂O₉ (A = Ca, Sr, Ba) prepared by the molten salt method were higher than those of the ABi₂Nb₂O₉ (A = Ca, Sr, Ba) prepared by traditional solid-state method, as shown in Table 9.

Shah *et al.* (2021) found that doped Mn atoms at active sites displayed a significant effect on reducing the overpotential of the oxygen evolution reaction (OER) of pristine BFO, BFO with Fe and Mn as active sites is 0.93, 0.60 and 0.51 V, respectively, and the optimum amount with Mn doping (0.05%) showed an OER activity of 255 μmol g⁻¹ h⁻¹ under visible light (λ ≥ 420 nm) irradiation.

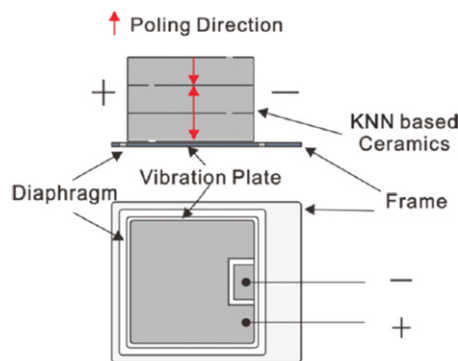


Fig. 18 Schematic diagram of the KNN-based flat panel piezoelectric micro speaker. Reproduced from Gao, R.L., Chu, X.C., Huan, Y., *et al.*, 2014. A study on (K, Na)NbO₃ based multilayer piezoelectric ceramics micro speaker. *Smart Materials and Structures* 23 (10), 105018, with the permission of IOP Publishing LTD.

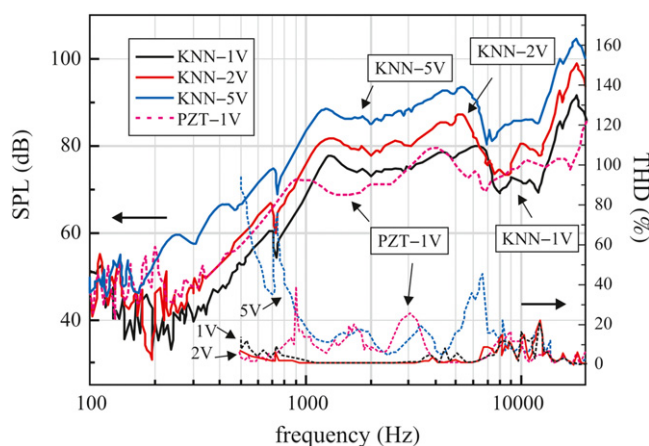


Fig. 19 SPL and THD curves of 30/3 under different drive voltages, compared with a PZT-based micro speaker under 1 Vrms. Reproduced from Gao, R.L., Chu, X.C., Huan, Y., *et al.*, 2014. A study on (K, Na)NbO₃ based multilayer piezoelectric ceramics micro speaker. *Smart Materials and Structures* 23 (10), 105018, with the permission of IOP Publishing LTD.

CO₂ photoreduction Tu *et al.* (2019) reported SrBi₄Ti₄O₁₅ ferroelectric nanosheets with large intrinsic polarization that originates from the distortion of TiO₆ octahedra along the polar *a* axis. The strong spontaneous polarization along the [100] direction rendered efficient separation and anisotropic migration of carriers, resulting in a powerful CO₂ reduction ability for CH₄ and CO production, far outperforming other catalysts. Particularly, CH₄ as the primary product shows a high-efficiency evolution rate of 19.8 μmol g⁻¹ h⁻¹ with a high selectivity of 93%, and the apparent quantum efficiency (AQE) is as high as 1.33% at 365 nm. The CH₄ evolution rate of SrBi₄Ti₄O₁₅ is ~8.65 and 283 times that of Bi₄Ti₃O₁₂ and BiOBr, respectively.

Zangeneh *et al.* (2020) designed BaTiO₃-Fe₂O₃ heterojunctions and the highest CO₂ conversion efficiency reached 22% in the presence of CH₄ as reducing agent within 60 min processing. The outstanding CO₂ conversion rate can be attributed to not only the efficient separation and immigration of photogenerated charge carriers but also the boosted light harvesting in the n-n heterojunction.

Future Directions

- (1) The relationship of micro-/nano-structures and properties of lead-free piezoelectric ceramics should be further studied to fully understand the nature of multifunctionality.
- (2) Due to the sintering characteristics of lead-free piezoelectric ceramics, the stability and repeatability of the process still need to be further improved;
- (3) The influence of the microstructure and properties of lead-free piezoelectric ceramics on the frequency sweep characteristics, temperature drift and linearity of the sensor needs to be further studied;
- (4) Continuing to find suitable doping elements or compounds to improve the piezoelectric properties of lead-free piezoelectric ceramics with high T_C , high k_p , high d_{33} or high T_C , high Q_m simultaneously.

Table 9 H₂ and O₂ evolution rates of ABi₂Nb₂O₉ (A = Ca, Sr, Ba). Powders prepared by different methods^a

Photocatalyst	H ₂ evolution rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	O ₂ evolution rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)
CBN(SSR) – 850/Pt	6.7	29.8
CBN(MSM) – 850	Not detected	112
CBN(MSM) – 850/Pt	104.1	69.4
SBN(SSR) – 850/Pt	0.9	15.7
SBN(MSM) – 850	Not detected	276.5
SBN(MSM) – 850/Pt	8.9	143.3
BBN(SSR) – 850/Pt	0.4	10.9
BBN(MSM) – 850	Not detected	11.2
BBN(MSM) – 850/Pt	6.2	13.3

^aReaction time 5 h. The content of the deposited Pt was 0.5 wt%. A 200 mL TEA solution (10 vol%) and a 20 mL AgNO₃ solution were used as sacrificial reagents for photoreduction and photooxidation, respectively. MSM-X : Molten salt method (where X represents the temperature of the molten salt); SSR: Solid-state reaction; Pt: Pt Cocatalyst.

Note: Reproduced from Zhang, Y., Yuan, J., Gong, H., *et al.*, 2018c. (001) Facet-exposed planelike ABi₂Nb₂O₉ (A = Ca, Sr, Ba) powders with a single-crystal grain for enhancement of photocatalytic activity. ACS Sustainable Chemistry Engineering 6, 3840 – 3852, with the permission of American Chemical Society.

- (5) Conformation of the key factors that can determine the “hard” (high coercive field, low permittivity and low dielectric losses) or “soft” (high dielectric losses, low conductivity, low coercive field and high piezoelectric coefficients) modifications in lead free piezoelectric ceramics;
- (6) For applications, mass-production and commercialization of lead-free piezoelectric ceramics should be taken into consideration.
- (7) How to obtain KNN based lead-free piezoelectric ceramics with high piezoelectric properties and high temperature stability at the same time;
- (8) It remains a challenge to improve the T_d and d_{33} of BNT-based materials simultaneously.
- (9) The coercive field of BLSFs and PLS piezoelectric ceramics is reduced to make the polarization easier.

Conclusions

In the past decades, the exciting progress has been achieved for the lead-free piezoelectric ceramics with good piezoelectric properties by optimizing composition, phase boundary and nanometer domains. Undoubtedly, the phase boundaries and domain configurations determine the piezoelectric effects of the most lead-free piezoelectric ceramics. For example, the new phase boundary, such as R-O-T, R-T, phase boundary, could be constructed at room temperature in KNN-based system. Enhanced piezoelectric properties in lead-free piezoelectric ceramics could be gained by ions or compounds substitution, the construction and types of phase boundaries near room temperature, and many other methods (sintering aids, synthesis technique, poling conditions, and so on). Some devices, such as nanogenerator, energy harvester, ultrasonic transducer, sensors, resonators, were made by lead-free piezoelectric ceramics; that reveals the promised and charming future of the commercialization of lead-free piezoelectric ceramics.

However, it was found that strong temperature, composition and processing dependence on the piezoelectric properties of lead-free piezoelectric ceramics, and the rather narrow sintered temperature for lead-free piezoelectric ceramics. The origin mechanism of the high piezoelectric properties of the lead-free piezoelectric ceramics still needs systematic investigations in the future. The developing higher performance with maintaining high T_C of lead-free piezoelectric ceramics has great potential for the future and is the key to success for the applications. The temperature sensitivity (especially for higher 600°C) of the electrical properties of the lead-free piezoelectric ceramics was not completely understood, which is not beneficial for practical applications (especially for higher 600°C). The large hysteresis and high driving electric field still hinder lead-free piezoelectric ceramics' practical applications. The strain value of the lead-free piezoelectric ceramics should be further improved. In the further research, much more attentions should be paid on the enhancement of comprehensive properties, property/structure evolution under external fields, detailed performance characterization of electronic devices, and so on. The lead-free piezoelectric ceramics shall have promising potentials to achieve practical applications in the future.

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Flexoelectric or Flexoelectric-Like Effect in Ceramics

Dongxia Tian, Institute of Advanced Materials, Hubei Normal University, Huangshi, China

Baojin Chu, CAS Key Laboratory of Materials for Energy Conversion and Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, China

Pan Chen, School of Energy Engineering, Huanghuai University, Zhumadian, China and Henan International Joint Laboratory of Structural Mechanics and Computational Simulation, Huanghuai University, Zhumadian, China

Xiuzhang Wang and Meifeng Liu, Institute of Advanced Materials, Hubei Normal University, Huangshi, China

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Abstract

The flexoelectric effect is an electromechanical effect existing in all dielectrics, where strain gradient generates electric polarization or electric field gradient generates mechanical stress. Through a lot of experimental research, it was found ferroelectric ceramics possess larger flexoelectric coefficients than other dielectric materials, which will be mainly discussed in this article. To make it easier to understand the flexoelectric response of ferroelectric ceramics, the article will primarily summarize the methods of measuring flexoelectric coefficients, and the magnitudes and the mechanisms of the measured flexoelectric coefficients of the ceramics. Finally, the perspective and some urgent questions to be solved will be pointed out.

Key Points

- The measurement methods of flexoelectric coefficients were mainly divided into bending and compression of asymmetric structure.
- The reported flexoelectric coefficients of ferroelectric ceramics were summarized.
- The reported mechanisms for the measured flexoelectric coefficient of ferroelectric materials were evaluated, which indicates spontaneously polarized surface in ferroelectric ceramics is the dominant mechanism for insulating ferroelectric ceramics.

Introduction

The polarization in dielectric materials can be from strain gradient, which is expressed as below (Cross, 2006).

$$P_i = \mu_{ijkl} \frac{\partial S_{kl}}{\partial x_j} \quad (1)$$

Where P_i is the electric polarization, S_{kl} is the strain, $\partial S_{kl}/\partial x_j$ is the strain gradient, and μ_{ijkl} is the flexoelectric coefficient (fourth rank tensor). The above equation describes the direct flexoelectric effect. There also exists a converse flexoelectric effect (CFE), as shown below (Cross, 2006),

$$T_{ij} = \mu_{ijkl} \frac{\partial E_k}{\partial x_l} \quad (2)$$

where T_{ij} is the induced stress, and $\partial E_k/\partial x_l$ is the electric field gradient.

The flexoelectric coefficient is a parameter to evaluate the magnitude of flexoelectric response. For centrosymmetric dielectric materials, the flexoelectric coefficient includes transverse flexoelectric coefficient (μ_{12}), longitudinal flexoelectric coefficient (μ_{11}), shear flexoelectric coefficient (μ_{14}) (Yudin and Tagantsev, 2013). It was proposed that the flexoelectric coefficient scales with the dielectric susceptibility of materials, which is written as (Tagantsev, 1991; Cross, 2006)

$$\mu_{ij} = \gamma \chi_{ij} \frac{e}{a} \quad (3)$$

Where χ_{ij} is the dielectric susceptibility, γ is the scaling factor, e is the electron charge and a is the unit cell dimension. According to the equation, the flexoelectric coefficients of simple dielectrics are in the order of $10^{-11} \sim 10^{-10}$ C. m⁻¹ (Cross, 2006; Tagantsev, 1991; Zubko *et al.*, 2013; Yudin and Tagantsev, 2013). In the early 2000s, a large flexoelectric coefficient at μ C. m⁻¹ level was measured in ferroelectric materials by Cross and coworkers, which attracted researchers' attention (Cross, 2006; Ma and Cross, 2001b,a, 2002, 2003; Yudin and Tagantsev, 2013; Zubko *et al.*, 2013; Zhou *et al.*, 2019a; Wang *et al.*, 2019). Meanwhile, a new issue that the measured flexoelectric coefficients of ferroelectric materials are much larger than the estimated values arose (Zubko *et al.*, 2013; Yudin and Tagantsev, 2013; Zhou *et al.*, 2019a). Several experimental results indicate the extrinsic mechanisms dominate the measured flexoelectric coefficients of ferroelectric materials (Zhou *et al.*, 2019a; Wang *et al.*, 2019).

In this article, we will summarize the measurement methods and measurement results of flexoelectric coefficients of different ferroelectric ceramics, and mechanisms for the measured flexoelectric coefficients, which will be presented in Section 2, 3 and 4, respectively. Finally, the prospective of this research field will be discussed in Section 5.

Measurement Methods of Flexoelectric Coefficients

In order to measure flexoelectric coefficients, some methods were used to generate strain gradient in the ceramics. The typical approaches to generate strain gradient include bending and compression of asymmetric structure (such as pyramid shape). In this section, we will describe how to measure flexoelectric coefficients.

Measurement of Flexoelectric Coefficients by Bending

To measure the transverse flexoelectric coefficients of ferroelectric ceramics, the bending deformation can be generated by cantilever bending (CB), four-point bending (4PB), three-point bending (3PB), and point-ring (PR).

The flexoelectric coefficient measured by the cantilever bending method (CB) is μ_{12} (Ma and Cross, 2002, 2001a,b). For a ceramic bar, one end is clamped and another free end is driven by a force (schematically shown in Fig. 1(a)), which causes an inhomogeneous displacement along the beam (i.e., bending deformation). The displacement is a function with the position x_1 (the distance from the clamping end) on the beam. The bending deformation induces strain gradient along the thickness direction (x_3). Several little circular electrodes are deposited along the beam, and the strain gradient $\partial S_{11}/\partial x_3$ can be written as below:

$$\frac{\partial S_{11}}{\partial x_3} = \frac{\partial^2 w(x_1)}{\partial x_1^2} \quad (4)$$

where $w(x_1)$ is the displacement of the point x_1 after bending, and is usually measured using a laser displacement sensor. The generated current (i) from flexoelectric response can be directly measured by a lock-in amplifier, and is transformed to the polarization (P) using the equation

$$P = \frac{i}{2\pi f A} \quad (5)$$

where f is the measurement frequency, and A is the electrode area. For each spot, the polarization from flexoelectric response is linearly proportional to the strain gradient. As shown in Fig. 2, the flexoelectric coefficient is the slope between the polarization and the strain gradient (Ma and Cross, 2002).

The usage of separate circular electrodes is appropriate for materials with large flexoelectric coefficients, but not for those with weak flexoelectric coefficients. Thus, the materials with weak flexoelectric coefficients need to be coated with electrode of a wider area (Fig. 1(a)). If the electrodes spread over both surfaces of a cantilever beam, the μ_{12} can be derived using the linear ratio coefficient between i and $w(x_1)$ (Chu and Salem, 2012):

$$i = \frac{2\pi f \mu_{12} b L}{x_1^2 [1 - (x_1/3L)]} w(x_1) \quad (6)$$

where b is the width of the beam, L is the length of the beam.

The four-point bending (4PB) method was also used to measure μ_{12} . As schematically shown in Fig. 1(b), for a rectangular sample, both ends of the bottom side are supported by metal bars, and two forces from the top metal bars compress the samples,

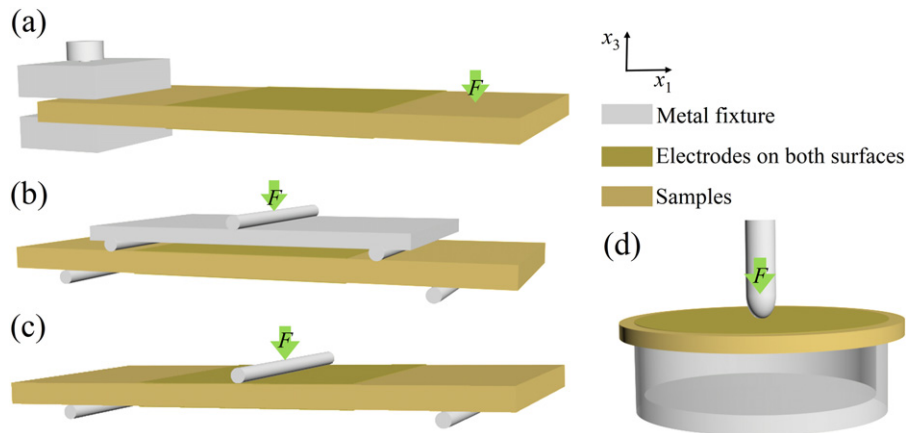


Fig. 1 The schematics of (a) cantilever bending, (b) four-point bending, (c) three-point bending and (d) point-ring methods applying strain gradient during the measurement of flexoelectric coefficient.

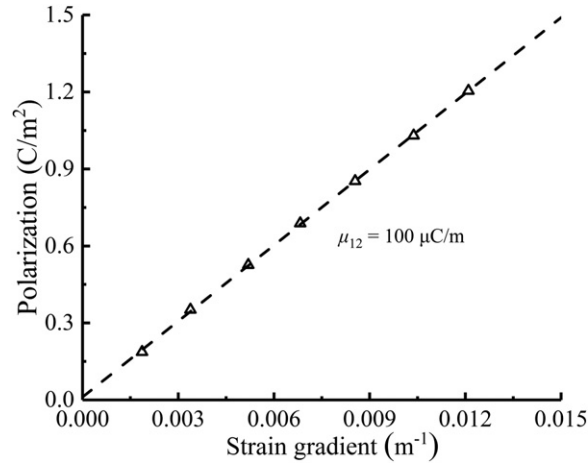


Fig. 2 The relationship between flexoelectric polarization and strain gradient in Ba_{0.67}Sr_{0.33}TiO₃ ceramics. Reproduced from Ma, W., Cross, L.E., 2002. Flexoelectric polarization of barium strontium titanate in the paraelectric state. *Applied Physics Letters* 81, 3440–3442, with the permission of AIP Publishing.

which produces a strain gradient $\partial S_{11}/\partial x_3$ along thickness direction, as calculated below (Ma and Cross, 2003):

$$\frac{\partial S_{11}}{\partial x_3} = \frac{12st}{L^2} \quad (7)$$

where s is the speed of the top metal bars, t is the time, and L is the distance of the outer span. The polarization from the strain gradient is

$$P = \frac{Q}{A} \quad (8)$$

where Q is the induced electric charge measured by an electrometer connecting the top and bottom electrodes. In this case, μ_{12} is derived to be

$$\mu_{12} = \frac{QL^2}{12Ast} \quad (9)$$

In contrast to the 4PB method, two point forces in the middle of the top side is reduced to one point force for the three-point bending method (3PB), as shown in Fig. 1(c). The 3PB can be applied using a dynamic mechanical analyzer (DMA) or modified d_{33} meter. For deformation provided by DMA, the generated polarization from flexoelectric response is also measured by a lock-in amplifier, and calculated using Eq. (5). The strain gradient in the thickness direction (x_3) is derived to be (Zubko *et al.*, 2007):

$$\frac{\partial S_{11}}{\partial x_3} = \frac{12z_0}{L^3}(L - 2x_1) \quad (10)$$

where z_0 is the displacement of the center point, and measured by the DMA. x_1 is the half length of the electrodes. Simultaneous Eqs. (5) and (10), the μ_{12} is written to be

$$\mu_{12} = \frac{iL^3}{48\pi f b x_1 z_0 (L - 2x_1)} \quad (11)$$

If the 3PB test fixture is installed on a d_{33} meter, a d_{33} constant from flexoelectric response can be measured in unpolarized materials. The relationship between μ_{12} and d_{33} can be given by Chu *et al.* (2011):

$$d_{33} = \frac{3\mu_{12}(1 - \sigma)L^2}{2h^3c_{11}} \quad (12)$$

where σ is the Poisson ratio of ceramics, h is the thickness, and c_{11} is the elastic modulus. It can be noted that the 3PB test mode using a d_{33} meter is more convenient than that using a DMA. However, the measured frequency of a d_{33} meter is fixed due to the instrument design.

The aforementioned methods are used to measure rectangular ceramics. The point-ring method (PR) was used for disc ceramics. As shown in Fig. 1(d), one side of a disc sample is supported by a metal ring with comparable inner diameter, and the middle of the other side is applied a force (F), which causes a bending deformation. The generating strain gradient in the thickness direction (x_3 direction) can be expressed as Zhang *et al.* (2016):

$$\frac{\partial S(r)}{\partial x_3} = \frac{3F(1 - \sigma^2)}{\pi c_{11} h^3} \left(\frac{\sigma}{1 + \sigma} + \ln \frac{r}{R} \right) \quad (13)$$

Where $S(r)$ is the strain along the radial direction, r is the distance of a point from the center of the disc, and R is the radius of the electrodes. The test fixture can also be installed on a d_{33} meter. The electric charge Q from the flexoelectric response can be

measured by the d_{33} meter.

$$d_{33} = \frac{Q}{F} \quad (14)$$

and the relationship between Q and flexoelectric coefficient is

$$Q = 2\pi \int_0^R \mu_p \frac{\partial S(r)}{\partial x_3} r dr \quad (15)$$

Here μ_p is the effective flexoelectric coefficient, and comprises the contribution of μ_{12} and μ_{11} . Substituting the Eqs. (13) and (14) into (15), the μ_p is derived to be:

$$\mu_p = \frac{2d_{33}c_{11}h^3}{3(1-\sigma)^2R^2} \quad (16)$$

Pyramid Compression (PC)

Besides through bending deformation described above, the strain gradient can also be produced through applying symmetric force to a ceramic with asymmetric shape, such as truncated pyramid-like shape, as shown in Fig. 3, and the longitudinal flexoelectric coefficient μ_{11} is measured. In this case, the generated strain S_{33} varies along the thickness direction (x_3) due to the asymmetric shape of the ceramic, namely a strain gradient along that direction. If the strain gradient $\partial S_{33}/\partial x_3$ is uniform, it can give (Cross, 2006):

$$\frac{\partial S_{33}}{\partial x_3} = \frac{[(F/c_{11}a^2) - (F/c_{11}b^2)]}{h} = \frac{F(b^2 - a^2)}{c_{11}a^2b^2h} \quad (17)$$

where a and b are the sides lengths of the top and bottom square surfaces, respectively. After measuring the generated polarization from flexoelectric response, the μ_{11} can be calculated. The method is not applicable for the materials with a piezoelectric response. Otherwise, the piezoelectric response would be included in the measured flexoelectric response (Biancoli *et al.*, 2015). Thus, the contribution from piezoelectric response should be first precluded experimentally when measuring flexoelectric coefficients using the PC method.

Measurement Results of Flexoelectric Coefficients

Flexoelectric coefficients of different ferroelectric ceramics were measured using the above methods, and Table 1 summarizes the flexoelectric coefficients of the ceramics. It should be emphasized that the measured flexoelectric coefficient is actually effective values, which contains extrinsic contributions (Discussed in next section) and some inseparable non-zero components (Biancoli *et al.*, 2015). For example, the measured μ_{11} includes the contribution of μ_{11} and μ_{12} . From Table 1, it can be noted that the flexoelectric coefficients vary with the measurement methods for the same material. Thus, the comparison of flexoelectric coefficients should be based on the same measurement method. The flexoelectric coefficients of BST ferroelectric ceramics are overall larger than that of Pb-containing ferroelectric ceramics (Cross, 2006; Ma and Cross, 2001b, 2002, 2003; Henmi and Tohyama, 2011; Ma and Cross, 2006; Zhang *et al.*, 2018; Chu *et al.*, 2009; Hou *et al.*, 2020; Tian *et al.*, 2021).

In order to enhance flexoelectric coefficients, composite or doping approach is adopted (Li *et al.*, 2014; Shu *et al.*, 2017; Li *et al.*, 2019). After doping 0.5 wt% Al_2O_3 into $\text{BaTi}_{0.85}\text{Sn}_{0.15}\text{O}_3$ ceramics, the flexoelectric coefficient becomes double (Shu *et al.*, 2017). In our research group, it was found that reduction reaction using graphite or thermal treatment can greatly enhance the flexoelectric coefficient of ferroelectric ceramics (Zhou *et al.*, 2015, 2016; Zhou and Chu, 2017; Zhou *et al.*, 2018; Zhang and Chu, 2018;

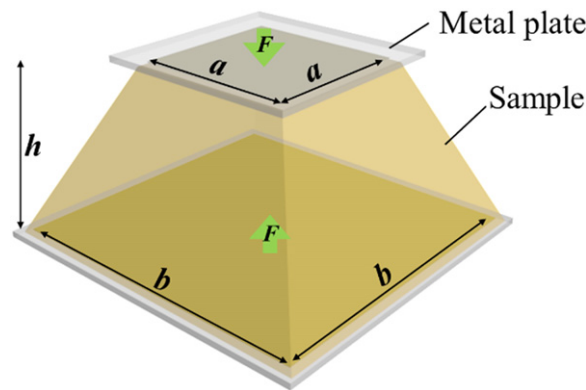


Fig. 3 The schematic of a pyramid compression applying strain gradient when the flexoelectric coefficient is measured.

Zhang *et al.*, 2018; Zhou *et al.*, 2019b; Tian *et al.*, 2021). For example, the effective flexoelectric coefficient of reduced $0.92\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.08\text{BaTiO}_3$ (NBBT8) can be increased to more than $1.8 \text{ mC} \cdot \text{m}^{-1}$, which is almost two orders of magnitude than that without a reduction reaction (Zhang and Chu, 2018). The high values of the reduced ceramics can be maintained at a high temperature (Zhang and Chu, 2018).

Compound $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ is abbreviated as PMN, PbTiO_3 is abbreviated as PT, $\text{Pb}(\text{Zr,Ti})\text{O}_3$ is abbreviated as PZT. Compound $1-x(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-}x\text{BaTiO}_3$ is abbreviated as NBT(100x).

Mechanism for the Measured Flexoelectric Coefficient of Ferroelectric Materials

Theoretical study indicates that for flexoelectric effect, there should be four contributions, namely bulk dynamic flexoelectricity, bulk static flexoelectricity, surface flexoelectricity, and surface piezoelectricity (Cross, 2006). The bulk flexoelectricity and surface flexoelectricity are theoretically proportional to the permittivity of materials. Surface layers (several atoms thick) generate surface piezoelectricity, contributing to the flexoelectric response (Tagantsev, 1986; Tagantsev and Yurkov, 2012; Stengel, 2013; Stengel, 2014; Hong and Vanderbilt, 2011). The flexocoupling coefficient f_{sjkl} is also often used to evaluate the magnitude of the flexoelectric response, and is expressed below (Zubko *et al.*, 2013):

$$f_{sjkl} = \frac{\mu_{ijkl}}{\chi_{is}\epsilon_0} \quad (18)$$

where ϵ_0 is the vacuum permittivity. Theoretically, if f_{sjkl} is generated by intrinsic lattice contribution, it should be lower than 15 V for materials with perovskite structure (Zubko *et al.*, 2013). Otherwise, the perovskite structure should be unstable and induce incommensurate phases (Zubko *et al.*, 2013). For the experimental results, f_{sjkl} of ferroelectric materials is often several orders of magnitude larger than the theoretically estimated values (Hou *et al.*, 2020; Tian *et al.*, 2021; Zhang *et al.*, 2018; Pan *et al.*, 2019; Zhang and Chu, 2018; Zhou *et al.*, 2019b). The large discrepancy between measured and theoretical flexocoupling coefficients implies there are extrinsic mechanisms that dominate the flexoelectric response. Here, some proposed extrinsic mechanisms are summarized in this section.

In ferroelectric ceramics, it was found that there usually exists spontaneously polarized surfaces with approximately several μm in thickness, which is different from the theoretically predicted piezoelectric surface layer with a thickness of several atoms (Zhang *et al.*, 2018; Zhou *et al.*, 2019b; Zubko *et al.*, 2013; Yudin and Tagantsev, 2013). The spontaneously polarized surfaces are inevitably generated after ferroelectric ceramics slowly cooled from a temperature of above T_C (Curie temperature) or T_m (the temperature of the highest permittivity). During the process of heat treatment, a phase transition between ferroelectrics and paraelectrics occurs, which causes a residual stress. During cooling from the high temperature, the grains on surfaces are constrained by the surrounding grains biaxially and can release the stress along the direction perpendicular to the surfaces. As a consequence, the stress in each surface with a thickness of $\sim 10 \mu\text{m}$ releases inhomogeneously, which causes a strain gradient and makes surfaces polarized. Under bending, a piezoelectric response from the polarized surfaces greatly contributes to the measured flexoelectric-like response of ferroelectric ceramics (Fig. 4 (a-b)) (Zhang *et al.*, 2018).

The polarization of the surfaces is hard to eliminate completely using the abrading or quenched method because it can recover easily during heating (Fig. 4(b)). After fired metal electrode pastes on the surfaces of ferroelectric ceramics at a high temperature, the polarized surfaces can be destroyed to a certain extent due to the electrode paste diffusing into the surface regions, stress relief, and the generation of impurity phases caused by volatile element evaporating at high temperature (Tian *et al.*, 2021). As a consequence, the suppressed polarized surfaces arouse a huge decay of the flexoelectric-like response when bending the ferroelectric ceramics (Tian *et al.*, 2021). For example, after suppressing polarized surfaces, the flexocoupling coefficients can approach the intrinsic coefficients for $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$ ceramics and $0.92\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.08\text{BaTiO}_3$ ceramics (Fig. 4 (c) and (d)), which demonstrated that the piezoelectric response from the polarized surfaces is the dominant mechanism causing the large deviation of the measured flexoelectric-like response from the intrinsic response in ferroelectric ceramics (Tian *et al.*, 2021).

Other flexoelectric mechanisms were used to explain the large flexoelectric response of ferroelectric materials.

For relaxor ferroelectrics, it was thought that the strain gradient makes the preexisting nanodomains or nanopolar regions have a preferable orientation, contributing to the large flexoelectric response (Fig. 5) (Ma and Cross, 2001a; Narvaez and Catalan, 2014). However, the flexoelectric mechanism is just targeted at relaxor ferroelectrics, not for common ferroelectrics. Furthermore, how much the nanodomain contribution to the flexoelectric response is unclear.

The discrepancy between measured and theoretical flexoelectric response was also ascribed to sample processing causing symmetry breaking (Biancoli *et al.*, 2015). During densifying ceramics, the charged defects and polar nano-entities redistribute according to the setting position and direction of the samples and sintering temperature, which determines the orientation of the built-in polarization. The piezoelectric response from the built-in polarization enhances the measured flexoelectric response. If the mechanism is the main source of the large flexoelectric response of ferroelectric materials, the flexoelectric coefficients of the same ceramics prepared by different research groups should be different due to inconsistent processing conditions. However, the reported ceramics with the same compositions have a consistent flexoelectric coefficient measured by the same method.

The above mechanisms for explaining the large deviation of the measured flexoelectric response from theoretical response were proposed for insulating ferroelectric materials. For semiconductors, a larger flexoelectric coefficient than that in their insulating ferroelectric materials was measured, and a barrier-layer mechanism was used to explain the large flexoelectric-like response

Table 1 A summary of the measured flexoelectric coefficients of ferroelectric ceramics at room temperature

Materials	Flexoelectric coefficient (frequency)	Value ($\mu\text{C} \cdot \text{m}^{-1}$)	Methods
Ba _{0.67} Sr _{0.33} TiO ₃ (Cross, 2006)	μ_{11} (0.5 Hz)	150	PC
Ba _{0.67} Sr _{0.33} TiO ₃ (Fu <i>et al.</i> , 2006)	μ_{11} (400 Hz)	121	CFE
Ba _{0.67} Sr _{0.33} TiO ₃ (Ma and Cross, 2002)	μ_{12} (1 Hz)	100	CB
Ba _{0.67} Sr _{0.33} TiO ₃ (Shu <i>et al.</i> , 2014)	μ_{12} (10 Hz)	124 $\pm$ 14	CFE
Ba _{0.67} Sr _{0.33} TiO ₃ (Hou <i>et al.</i> , 2020)	μ_{ρ} (110 Hz)	284	PR
Ba _{0.67} Sr _{0.33} TiO ₃ (Chu <i>et al.</i> , 2009)	μ_{12}	6–10	3PB
Ba _{0.65} Sr _{0.35} TiO ₃ (Huang <i>et al.</i> , 2011)	μ_{12} (2 Hz)	8.5	CB
Ba _{0.6} Sr _{0.4} TiO ₃ (Zhang <i>et al.</i> , 2016)	μ_{ρ} (110 Hz)	10	PR
Ba _{0.6} Sr _{0.4} TiO ₃ (Li <i>et al.</i> , 2014)	μ_{12} (30 Hz)	100	CB
Ba _{0.6} Sr _{0.4} TiO ₃ /Ni _{0.8} Zn _{0.2} Fe ₂ O ₄ (Li <i>et al.</i> , 2014)	μ_{12} (30 Hz)	128	CB
Ba _{0.5} Sr _{0.5} TiO ₃ (Hou <i>et al.</i> , 2020)	μ_{ρ} (110 Hz)	2	PR
SrTiO ₃ (Hou <i>et al.</i> , 2020)	μ_{ρ} (110 Hz)	0.3	PR
SrTiO ₃ (Dai <i>et al.</i> , 2021)	μ_{12} (9 Hz)	0.008	CB
20% C doped SrTiO ₃ (Dai <i>et al.</i> , 2021)	μ_{12} (9 Hz)	0.159	CB
Ba _{0.75} Sr _{0.25} TiO ₃ (Tian <i>et al.</i> , 2021)	μ_{ρ} (110 Hz)	120	PR
BaTiO ₃ (Ma and Cross, 2006)	μ_{12}	10	CB
As prepared BaTiO ₃ (Zhang <i>et al.</i> , 2018)	μ_{ρ} (110 Hz)	120	PR
Abraded BaTiO ₃ (Zhang <i>et al.</i> , 2018)	μ_{ρ} (110 Hz)	30	PR
Quenched BaTiO ₃ (Zhang <i>et al.</i> , 2018)	μ_{ρ} (110 Hz)	45	PR
Heat-treated BaTiO ₃ (Zhang <i>et al.</i> , 2018)	μ_{ρ} (110 Hz)	~ 200	PR
BaTiO ₃ -0.08Bi(Zn _{0.5} Ti _{0.5})O ₃ (Huang <i>et al.</i> , 2017)	μ_{12} (20 Hz)	~ 25	CB
BaTi _{0.87} Sn _{0.13} O ₃ (Shu <i>et al.</i> , 2013)	μ_{12} (30 Hz)	53	CB
BaTi _{0.85} Sn _{0.15} O ₃ (Shu <i>et al.</i> , 2017)	μ_{12} (10 Hz)	~ 18	CB
0.5 wt%Al ₂ O ₃ -doped BaTi _{0.85} Sn _{0.15} O ₃ (Shu <i>et al.</i> , 2017)	μ_{12} (10 Hz)	40.5	CB
0.2 wt%Al ₂ O ₃ -doped BaTi _{0.85} Sn _{0.15} O ₃ (Shu <i>et al.</i> , 2017)	μ_{12} (10 Hz)	2	CB
(Pb _{0.3} Sr _{0.7})TiO ₃ (Cross, 2006)	μ_{11} (0.5 Hz)	21	PC
PMN (Ma and Cross, 2001b)	μ_{12} (1 Hz)	4	CB
0.9PMN-0.1PT (Hana, 2007)	μ_{11}	6–12	PC
0.9PMN-0.1PT (Hana, 2007)	μ_{11}	20–50	PC
0.9PMN-0.1PT (Hana <i>et al.</i> , 2011)	μ_{33} (0.2 Hz)	~ 1000	CFE
2.5%Bi-doped 0.7PMN-0.3PT (Li <i>et al.</i> , 2019)	μ_{12} (7 Hz)	260	CB
2.5%Bi-doped 0.68PMN-0.32PT (Li <i>et al.</i> , 2019)	μ_{12} (7 Hz)	300	CB
2.5%Bi-doped 0.66PMN-0.34PT (Li <i>et al.</i> , 2019)	μ_{12} (7 Hz)	220	CB
2.5%Bi-doped 0.64PMN-0.36PT (Li <i>et al.</i> , 2019)	μ_{12} (7 Hz)	80	CB
2.5%Sm-doped 0.70PMN-0.30PT (Yu <i>et al.</i> , 2021)	μ_{12}	430	CB
2.5%Sm-doped 0.68PMN-0.32PT (Yu <i>et al.</i> , 2021)	μ_{12}	550	CB
2.5%Sm-doped 0.66PMN-0.34PT (Yu <i>et al.</i> , 2021)	μ_{12}	490	CB
2.5%Eu-doped 0.66PMN-0.32PT (Yu <i>et al.</i> , 2021)	μ_{12}	380	CB
PZT (Ma and Cross, 2003)	μ_{12}	0.5 ~ 2	4PB
PZT (Ma and Cross, 2005)	μ_{12} (1 Hz)	1.4	CB
Abraded PZT-81 (Zhang <i>et al.</i> , 2018)	μ_{ρ} (110 Hz)	5	PR
Heat-treated PZT-81 (Zhang <i>et al.</i> , 2018)	μ_{ρ} (110 Hz)	~ 25	PR
Poled soft PZT (Henmi and Tohyama, 2011)	μ_{12} (0.5 Hz)	49	4PB
PbZrO ₃ (Vales-Castro <i>et al.</i> , 2018)	μ_{13}^{eff} (13 Hz)	~ 0.002	3PB
AgNbO ₃ (Vales-Castro <i>et al.</i> , 2018)	μ (13 Hz)	~ 0.005	3PB
NBT (Zhou <i>et al.</i> , 2019b)	μ_{ρ} (110 Hz)	0.43 $\pm$ 0.02	PR
NBBT2 (Zhou <i>et al.</i> , 2019b)	μ_{ρ} (110 Hz)	0.83 $\pm$ 0.14	PR
NBBT6 (Zhou <i>et al.</i> , 2019b; Zhang <i>et al.</i> , 2016)	μ_{ρ} (110 Hz)	6.1 $\pm$ 1.22	PR
NBBT8 (Zhou <i>et al.</i> , 2019b)	μ_{ρ} (110 Hz)	4.19 $\pm$ 0.49	PR
Heat-treated NBBT8 (Tian <i>et al.</i> , 2021)	μ_{ρ} (110 Hz)	20	PR
Reduced NBBT8 (Zhang and Chu, 2018)	μ_{ρ} (110 Hz)	1800	PR
NBBT10 (Zhou <i>et al.</i> , 2019b)	μ_{ρ} (110 Hz)	4.24 $\pm$ 0.95	PR
NBBT15 (Zhou <i>et al.</i> , 2019b)	μ_{ρ} (110 Hz)	3.29 $\pm$ 0.2	PR
NBBT20 (Zhou <i>et al.</i> , 2019b)	μ_{ρ} (11 0 Hz)	3.25 $\pm$ 0.38	PR
NBBT20 (Zhou <i>et al.</i> , 2015)	μ_{12}	2.4	CB
Reduced NBBT20 (Zhou <i>et al.</i> , 2015)	μ_{12}	100	CB
0.75BiFeO ₃ -0.25BaTiO ₃ (Pan <i>et al.</i> , 2019)	μ_{ρ} (110 Hz)	1	PR
Reduced 0.75BiFeO ₃ -0.25BaTiO ₃ (Pan <i>et al.</i> , 2019)	μ_{ρ} (110 Hz)	140	PR
(Bi _{1.5} Zn _{0.5})(Zn _{0.5} Nb _{1.5})O ₇ /Ag (Li <i>et al.</i> , 2013)	μ_{12} (10 Hz)	0.17	CB
(K _{0.4} Na _{0.58} Li _{0.02})(Nb _{0.96} Sb _{0.04})O ₃ (Zhu <i>et al.</i> , 2018)	μ_{12} (7 Hz)	1	CB

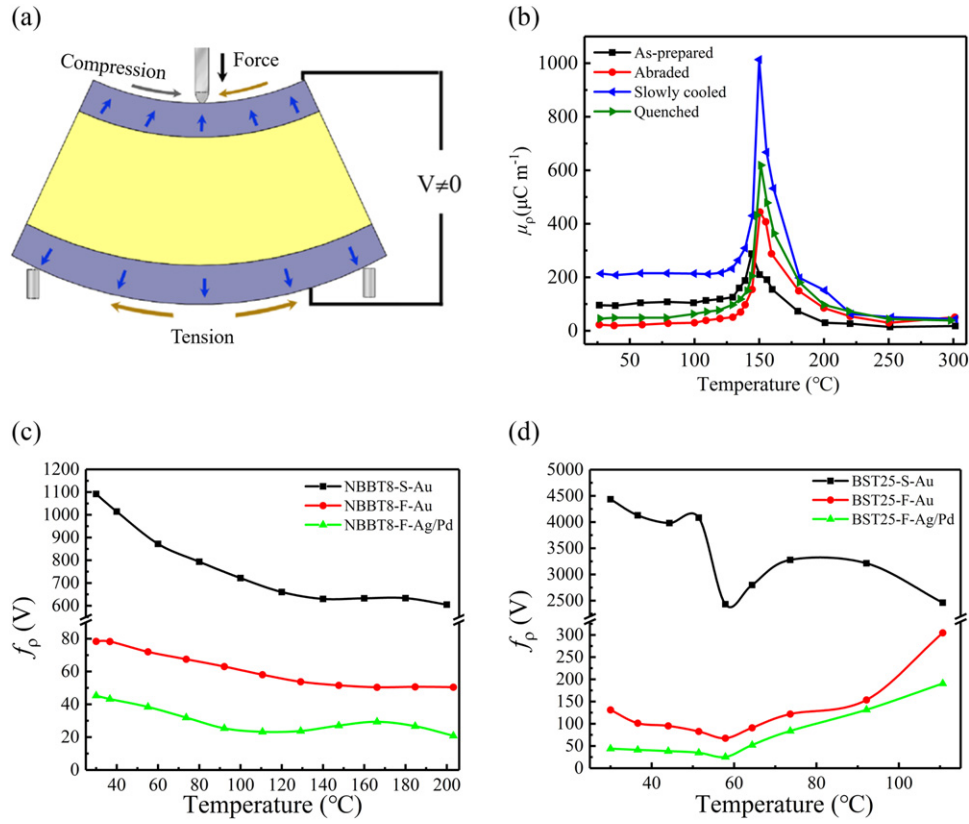


Fig. 4 (a) The schematic of the contribution of the spontaneously polarized surface to the measured flexoelectric-like response under bending. (b) (c) and (d) The flexocoupling coefficients of $0.92\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--}0.08\text{BaTiO}_3$ and $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$ ceramics after coating with sputtered (S) or fired on (F) electrodes. (b) The temperature dependence of flexoelectric coefficients of as-prepared, abraded, slowly cooled and quenched BaTiO_3 ceramics measured using PR method. The f_p is the effective flexocoupling coefficient. Reproduced from (a) Zhang, X., Pan, Q., Tian, D., *et al.*, 2018. Large flexoelectriclike response from the spontaneously polarized surfaces in ferroelectric ceramics. *Physics Review Letters* 121, 057602, with the permission of American Physical Society. (b) Tian, D., Hou, Y., Zhou, W., Chu, B., 2021. Flexoelectric response of ferroelectric ceramics with reduced surface layer effect. *Journal of Applied Physics* 129, 194103, with the permission of AIP Publishing.

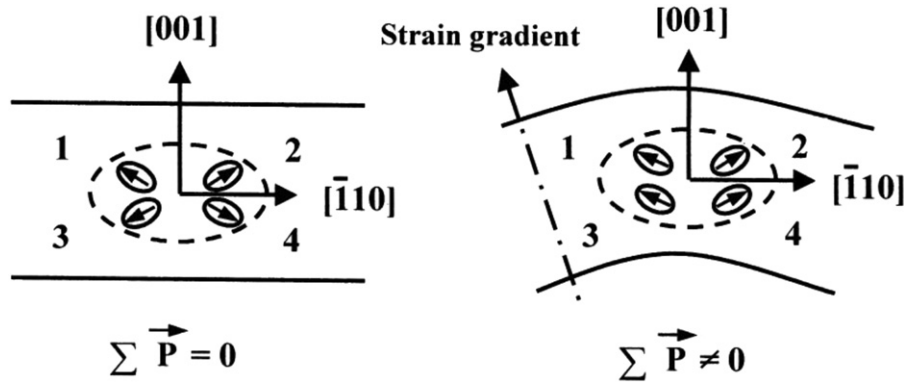


Fig. 5 The orientation of nanodomains of relaxor ferroelectrics before and after suffering from a strain gradient. Reproduced from Ma, W., Cross, L.E., 2001a. Large flexoelectric polarization in ceramic lead magnesium niobate. *Applied Physics Letters* 79, 4420–4422, with the permission of AIP Publishing.

(Narvaez *et al.*, 2016; Shu *et al.*, 2020; Dai *et al.*, 2021). The barrier layer mechanism enhancing flexoelectric-like response when bending the semiconductors (Narvaez *et al.*, 2016).

Some other factors also affect the flexoelectric response of ferroelectric materials. Beyond T_C , a residual ferroelectricity was put forward to explain the discrepancy between the estimated and measured flexoelectric coefficients (Garten and Trolrier-Mckinstry, 2015). Usually an inhomogeneous strain is generated near interfaces, such as interfaces between films and substrates, domain wall,

grain boundaries (Zubko *et al.*, 2007; Pertsev *et al.*, 2000; Wu *et al.*, 2022). The piezoelectricity of grain boundaries is also thought to be a non-negligible factor (Narvaez *et al.*, 2015). In materials, compositional heterogeneity, which can induce structural heterogeneity, is a method proposed to enhance flexoelectric response (Lee *et al.*, 2011; Zhou *et al.*, 2015; Yu *et al.*, 2021). In addition, the defects may also have an influence on flexoelectric response due to the pinning effect (Zhu *et al.*, 2018).

Summary and Future Trends

This article mainly summarizes the reported experimental results of flexoelectricity in ferroelectric ceramics. Though several measurement methods of flexoelectric coefficients have been designed, the method for measuring some non-zero components (such as shear flexoelectric coefficient) of flexoelectric coefficients of ferroelectric materials is still missing. From the reported flexoelectric coefficients, it can be seen that the measured flexoelectric coefficients are several orders of magnitude larger than the theoretical values for ferroelectric materials. The spontaneously polarized surface mechanism can explain this issue to a larger extent, other mechanisms may also contribute to the measured flexoelectric coefficients. Further study is required to thoroughly understand the mechanism of the large flexoelectric response of ferroelectric ceramics.

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Piezoelectric Ultrasonic Power Transducers

Tobias Hemsel, Faculty of Mechanical Engineering, Dynamics and Mechatronics, Paderborn University, Paderborn, Germany
Jens Twiefel, Institute of Dynamics and Vibration Research, Leibniz University Hannover, Garbsen, Germany

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Abstract

This article is dedicated to piezoelectric ultrasonic power transducers that differ to well known medical ultrasonic diagnostic apparatus or non destructive testing devices by the level of power in use; typically several tens of up to more than thousand watts are used in a multitude of different applications. After a short introduction including historical development, the first focus is on theoretical background of the operating principle, design and mechanical modeling. As piezoelectric elements transform electrical to mechanical energy and vice versa, equivalent circuit modeling is also described. After that, sample applications are delineated by the matter wherein ultrasound generates unique effects: incredible high pressure level as well in air as in water, micro-bubbles generating temperature peaks for very short time instances in fluids, acoustoplastic effect, enhancement of diffusion and recrystallization in solids, friction manipulation, incremental deformation and micro-cracking of surfaces, or even generation of macroscopic movements in motors. At the end, some future directions ranging from novel modeling approaches to advanced control and new materials are addressed.

Introduction

Piezoelectric ultrasonic power transducers differ from classical actuators by being driven at ultrasonic frequency (typically 20–2000 kHz) with rated electrical power of several tens up to some thousand watts. They are named "transducers" as both electrical-mechanical as well as mechanical-electrical energy conversion can be exploited. This article focusses on the electrical-mechanical energy conversion based on inverse piezoelectricity. After the first phenomenological and mathematical description of piezoelectricity at the end of the 19th century by (Curie and Curie, 1880; Lippmann, 1881) and exploiting the effects in measurement equipment (Curie, 1889), the first application of piezoelectric transducers using higher power amount was the active sonar based on (Langevin, 1918), wherein the functionally needed large sized piezoelectric crystal was replaced by mosaics of single smaller crystals and added metal layers. This application and later on ultrasonic cleaning were the main driver for the development of technically and economically valuable piezoelectric materials, leading finally to lead-titanate-zirconate ceramics (PZT), which are still the standard material today, (Jaffe *et al.*, 1954; Crawford, 1961). Typically, these brittle ceramics are sandwiched between metal elements by compressing bolts to achieve a highly dynamic vibration source called "Bolted Langevin Transducer" (Crawford, 1963).

With improved material design and power electronics, technical use of power ultrasound spread widely; it could easily fill a book on its own to display and declare all applications in detail. Instead of this, this article focuses on how to design ultrasonic power transducers, how to model and operate them. Basic ultrasound induced effects and their technical use will be described and a short glance on current research will be given.

Fundamentals on Piezoelectric Ultrasonic Power Transducers and Systems

This section covers the fundamentals necessary to understand and roughly design ultrasonic components, focusing the transducer itself. A typical system consists of the power converter, also named transducer, to convert electrical energy to mechanical energy. Further a booster typically is used for mechanical impedance matching, or in other words to adopt the vibration amplitude. Finally, a sonotrode – the tool – is the interface to the process.

Design and Mechanical Modeling

Typically, engineering design software tools cover those aspects which the user is mainly interested in: electrical engineers work on electrical networks, mechanical engineers on drawings. As piezoelectricity couples electrical and mechanical quantities, more comprehensive tools are needed to design excellent working systems. Several commercial tools allow for the calculation of coupled field problems. Ultrasonic transducers can be designed in detail using these tools, but to understand the basics of ultrasonic systems, a simplified one-dimensional approach is purposeful.

Many of the known ultrasonic power transducers can be viewed to be slender rods, mainly vibrating in their axial direction. The well-known wave equation for this case is

$$\ddot{u}(x, t) = c_0^2 u''(x, t) \quad (1)$$

with the speed of sound c_0 for long and thin structures and the local displacement u dependent on time t and location x , see e.g., (Inman, 2022). The dots indicate the time derivative and the prime indicates the location derivative. For a uniform rod and assumption of harmonic vibration the solution for arbitrary boundary conditions is:

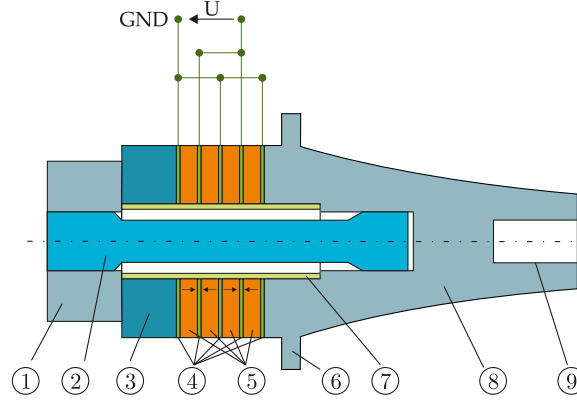


Fig. 1 Transducer: 1) nut, 2) bolt, 3) end-mass, 4) electrodes, 5) piezoelectric disks, 6) support, 7) centering element, 8) front-mass with amplitude adoption, 9) connection to booster or sonotrode.

$$\begin{pmatrix} \hat{v}_R \\ \hat{F}_R \end{pmatrix} = \begin{pmatrix} \cos(\kappa \uparrow) & \frac{j}{Z} \sin(\kappa \uparrow) \\ jZ \sin(\kappa \uparrow) & \cos(\kappa \uparrow) \end{pmatrix} \begin{pmatrix} \hat{v}_L \\ \hat{F}_L \end{pmatrix} = \mathbf{T}_{\text{rod}} \begin{pmatrix} \hat{v}_L \\ \hat{F}_L \end{pmatrix} \quad (2)$$

with the complex force and velocity amplitudes $\hat{F}$ and $\hat{v}$ at the left (index L) and right (index R) border of the rod. The complex amplitude $\hat{\cdot}$ contains the amplitude ($\cdot$) and phase φ information of a harmonic signal. The time dependent quantities are calculated by building the real part, e. g. for force: $F(t) = \text{Re}(\hat{F}e^{j\varphi}e^{j\Omega t}) = \text{Re}(\hat{F}e^{j\Omega t})$ with the angular excitation frequency Ω . $\kappa = \frac{\Omega}{c_0}$ is the wave number, $\uparrow$ the length of the rod and $Z = \rho c_0 A$ the impedance of the rod with the density ρ and the cross section A . The complex unit is indicated by j . To consider damping, a complex compliance $c_{33} = c_{33} \left(1 + j\frac{1}{Q_m}\right)$ is defined based on the quality factor Q_m ; this affects the speed of sound $c_0^2 = \frac{c_{33}}{\rho}$, the wave number and the impedance. The matrix $\mathbf{T}_{\text{rod}}$ is called transfer matrix for a rod (Pestel and Leckie, 1963). The resonance condition for a free-free rod with $\hat{F}_L = \hat{F}_R = 0$ is easily found with $\sin(\kappa \uparrow) = 0$. Consequently the angular resonance frequencies are $\omega_i = \frac{i c_0 \pi}{\uparrow}$ for $i = 1 \dots n$. At these resonance frequencies, the vibration shape of the free-free rod is a cosine with wavelength $\lambda_i = \frac{2\uparrow}{i}$.

Using transfer matrices, a more complex shaped rod can be computed by concatenation of multiple transfer matrices. The definition of the force and velocity direction guarantees that the left state is equal to the connected right state. Consequently, the problem can be solved by multiplying the transfer matrices, e.g., for three segments:

$$\begin{pmatrix} \hat{v}_R \\ \hat{F}_R \end{pmatrix} = \mathbf{T}_{\text{rod}(3)} \mathbf{T}_{\text{rod}(2)} \mathbf{T}_{\text{rod}(1)} \begin{pmatrix} \hat{v}_L \\ \hat{F}_L \end{pmatrix}. \quad (3)$$

For the design of ultrasonic power transducers, the piezoelectric coupling needs to be considered. Neglecting the well known anisotropic and often nonlinear behavior, a one-dimensional linear model again is the simplest and normally sufficient approach. Assuming that all stresses and dielectric displacements beside the (actuation) 3-direction are zero and that the dielectric displacement is constant in 3-direction leads to further simplification. The one dimensional coupled material equations are

$$E_3 = -\frac{d_{33}}{\epsilon_{33}^T} T_3 + \frac{1}{\epsilon_{33}^T} D_3, \text{ and} \quad (4)$$

$$S_3 = s_{33}^D T_3 + \frac{d_{33}}{\epsilon_{33}^T} D_3. \quad (5)$$

Here E_3 is the applied electric field, ϵ_{33}^T the corresponding permittivity at constant mechanical stress, D_3 the dielectric displacement (all in actuation direction). S_3 is mechanical strain, T_3 mechanical stress, s_{33}^D the compliance at constant dielectric displacement. The piezoelectric coupling is denoted by d_{33} , which is defined by mechanical strain per electric field at constant mechanical stress. The speed of sound is $c_0^2 = \frac{1}{s_{33}^D \rho}$.

Analog to the description of passive parts above, the transfer matrix is found as

$$\begin{pmatrix} \hat{v}_R \\ \hat{F}_R \\ \hat{U} \end{pmatrix} = \mathbf{T}_{\text{pzt}} \begin{pmatrix} \hat{v}_L \\ \hat{F}_L \\ \hat{I} \end{pmatrix}, \quad (6)$$

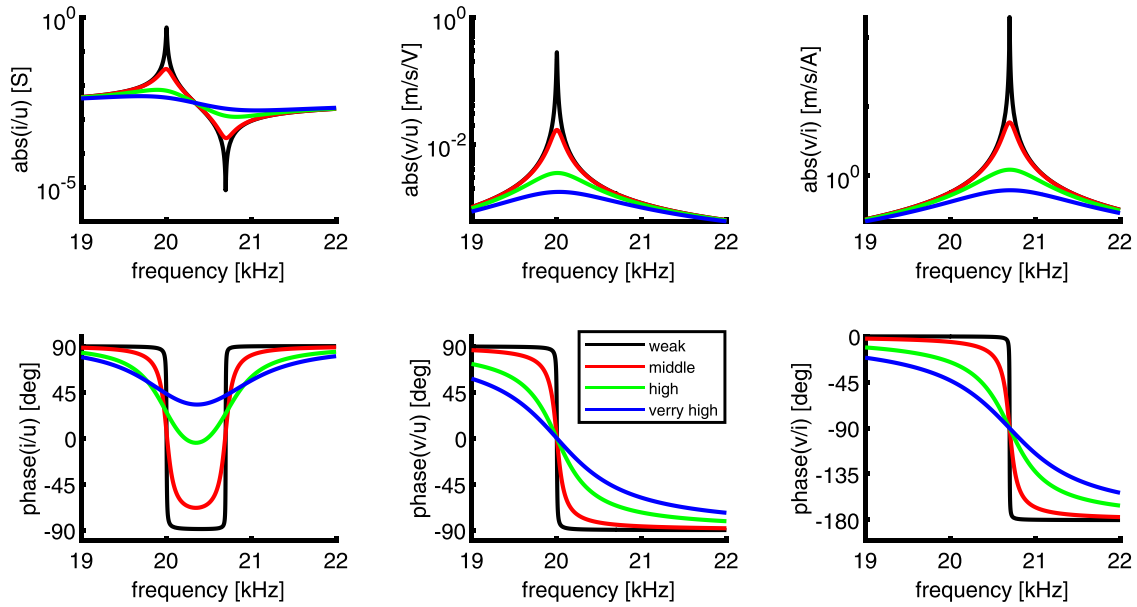


Fig. 2 Typical frequency response of an 20 kHz ultrasonic power transducer. The magnitudes are plotted on a logarithmic y-axis. The colors indicate: weak damping – black, middle damping – red, high damping – green, and very high damping – blue.

$$T_{\text{pzt}} = \begin{pmatrix} \cos(\kappa \uparrow) & \frac{j}{Z} \sin(\kappa \uparrow) & \frac{1}{Z\Omega d_{33}} \sin(\kappa \uparrow) \\ jZ \sin(\kappa \uparrow) & \cos(\kappa \uparrow) & \frac{1}{j\Omega d_{33}} (\cos(\kappa \uparrow) - 1) \\ -\frac{1}{j\Omega d_{33}} (\cos(\kappa \uparrow) - 1) & -\frac{1}{Z\Omega d_{33}} \sin(\kappa \uparrow) & \frac{1}{j\Omega C_p} \left(1 - \frac{k^2}{1 + k^2} \frac{1}{\kappa \uparrow} \sin(\kappa \uparrow)\right) \end{pmatrix} \quad (7)$$

now completed by electric voltage U and current i for the active piezoelectric element. $C_p = \varepsilon_{33}^T \frac{A}{l} \frac{1}{1+k^2}$ denotes the electric capacitance at constant strain and $k^2 = \frac{d_{33}^2}{\varepsilon_{33}^T \frac{A}{l}}$ the square coupling factor. After adopting the different sizes of the transfer matrices of piezoelectric and passive rods, resonance frequencies and vibration shapes for whole transducer systems can be computed. A numerically very effective method is given by [Nagem and Williams \(1989\)](#).

A sketch of a typical power ultrasonic transducer is given in [Fig. 1](#). A stack of an even number of piezoelectric disks – in this case 4 – is clamped by a bolt between the front- and end-masses. The piezoelectric disks are arranged with alternating polarization direction. The total length of the transducer determines its longitudinal resonance frequencies. By adjusting the lengths of passive and piezoelectric parts to the frequency and material dependent wavelengths of the used materials, the vibration shape can be designed appropriate to desired applications. The position of the piezoelectric stack defines the electro-mechanical coupling; the highest can be obtained in the central position of the half- λ vibration shape of the transducer, being operated at its first resonance. This position, however, is needed for the support of the transducer in the vibration node. Further, the mechanical load (stress and strain) is largest in this position (vibration node) as well, consequently the piezoelectric stack is located close to, but not in the vibration node, typically. The depicted transducer also includes a slight amplitude transformation: the front mass has a corresponding cross-section-shape and an approximate length of a quarter- λ . Due to their low electrical and mechanical losses "hard" piezoelectric materials (comparable to PZT-8) are commonly used for high power ultrasonic transducers, see chapter "High-Power Piezoelectric Materials" in this encyclopedia. Typical materials for front- and back-masses are titanium alloys and hardened steel.

A typical frequency response is given in [Fig. 2](#). The admittance (current i per voltage U) curve shows two peculiar frequencies. The resonance (the maximum magnitude) and the anti-resonance (the minimum magnitude) frequency are existing due to the piezoelectric coupling. At resonance, the piezoelectric elements are in short-circuited (very high current and very small voltage) condition, therefore its capacitance is not contributing to the effective stiffness of the piezoelectric elements. At anti-resonance the piezoelectric elements are in open-circuit conditions (very high voltage and very small current), here the capacitance is contributing to the effective stiffness. This change is quite large, the compliance is decreasing by approx. 40%; the effect on the frequency depends on the volume and position of the piezoelectric material. The higher the influence, the better the effective coupling is. However, the different stiffnesses change the vibration shape slightly (in typical transducer designs). The two electro-mechanical frequency responses (velocity v per voltage U or per current i) show that at both frequencies (resonance and anti-resonance) a large vibration amplitude can be obtained for a small electrical input. This is desired in the most power ultrasonic applications, consequently these two frequencies are common operation frequencies. Beside the large vibration amplitude both frequencies provide the advantage that the phase of the electrical admittance is zero (or at least close to), therefore the apparent input power equals (nearly) the effective input power, which benefacts the easy design of the needed power electronics.

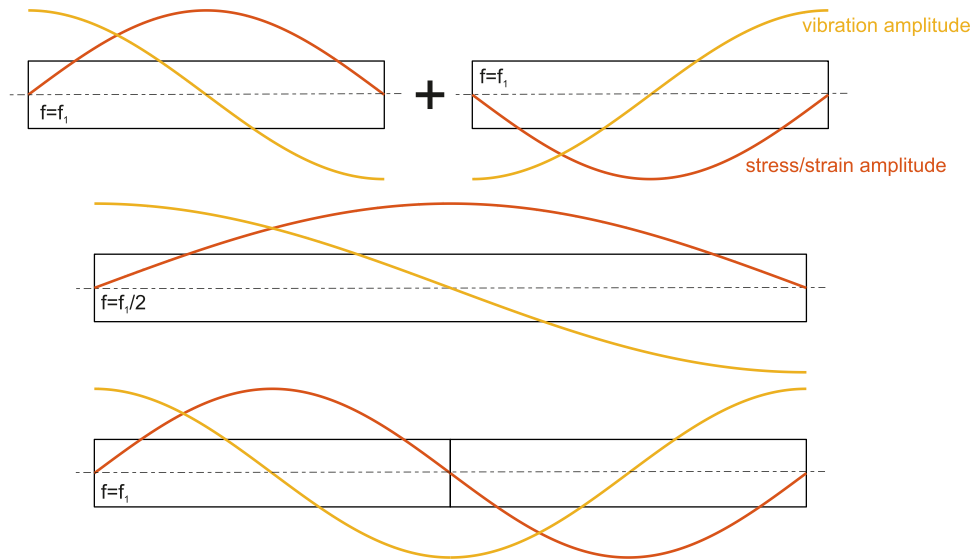


Fig. 3 Principle sketch of the half-wavelength synthesis concept, here combination of uniform rods.

Unfortunately, resonance and anti-resonance frequency are not constant due to changing load, aging, fatigue, temperature, strain and stress conditions. Hence a control of the operation frequency – see (Littmann *et al.*, 2003; Aldrich *et al.*, 2006; Twiefel *et al.*, 2008; Giraud *et al.*, 2014; Ille and Twiefel, 2015) – is needed to remain at the wanted vibration shape and vibration amplitude and to profit from small reactive power. Additionally, damping is affecting the frequency response, mainly due to the process. For high and very high damping loads, the phase response of the admittance no longer has a zero crossing. In this case an operation at the minimum phase has advantages. The use of tuned parallel or serial inductors can compensate the piezoelectric capacitance in near resonance or anti-resonance frequency respectively. This maintains phase zero crossing even for high damping situations. It is noteworthy in Fig. 2, that the ratio of velocity to current at the resonance frequency remains nearly unchanged for the various loading situations, the same applies for the ratio of velocity to voltage at anti-resonance. Thus, during operation at resonance or anti-resonance, the vibration amplitude even under load can well be estimated based on electrical measurements only.

For the design of power ultrasonic systems, the so-called *half-wavelength synthesis* is an important concept: it allows the (nearly) independent component design of transducers, boosters, and sonotrodes. In the case of a free-free component, the complex force amplitudes at the boundaries are zero, this allows the pairing with a second component, designed also for free-free conditions for the same resonance frequency. The resulting system provides a resonance at the same frequency as the single coupled components. However, due to the combination of the parts a new system is created. This has new eigenmodes and frequencies, that are in general not combinations of the modes of the joint parts. Only for the special case that both parts provide an eigenmode with very similar vibration distribution in the coupling area at the same frequency, the concept is applicable. Fortunately, this is often the case in power ultrasonic systems. The basic idea is illustrated in Fig. 3. Utilizing the simplified one-dimensional model the synthesis works perfectly, but also in the more complicated real case this is a commonly applied method.

For the power transfer towards the process, a proper impedance matching is the key. For the best power transfer the impedances should be (nearly) equal. On the electrical side a classical power transformer can be used to match the amplifier and the electrical input of the transducer. Further matching on the mechanical side can be designed using geometry and material selection. The vibration shape depends strongly on the material and cross-section profile of the rod. By reducing the cross section at a vibration nodal plane, vibration amplitude is enlarged and force amplitude lowered, leading to the name "booster" for such impedance matching parts of the vibrating system. The drawback of so-called "stepped horns" is the jump of the stress at the nodal plane. Hence, other shapes like exponential, linear, or conical cross-section profile are used, see Fig. 4. Their smoother stress profile comes with a smaller impedance change and thus smaller vibration amplitude magnification. For a half-wavelength booster, the vibration amplitude increases if the transducer side cross-section of the booster is larger than the sonotrode side cross-section. The force amplitude decreases at the same time; consequently, with more amplitude transformation, the ultrasonic system gets more sensitive on variations of the process dependent load.

Equivalent Circuit Modeling

Another very common kind of description for ultrasonic systems is equivalent circuit modeling. This is typically used to describe the electro-mechanical behavior from an electrical point of view. The generated electrical networks are helpful for system understanding, design of control strategies, and selection/design of power electronics.

The models are based on lumped parameters that describe the system's behavior in the operation regime. In the case of power ultrasonic systems this is typically the frequency range around resonance and anti-resonance. From the mechanical view point it covers the behavior of the selected dominant vibration mode. Therefore, it is a so-called modal model. Electro-mechanical

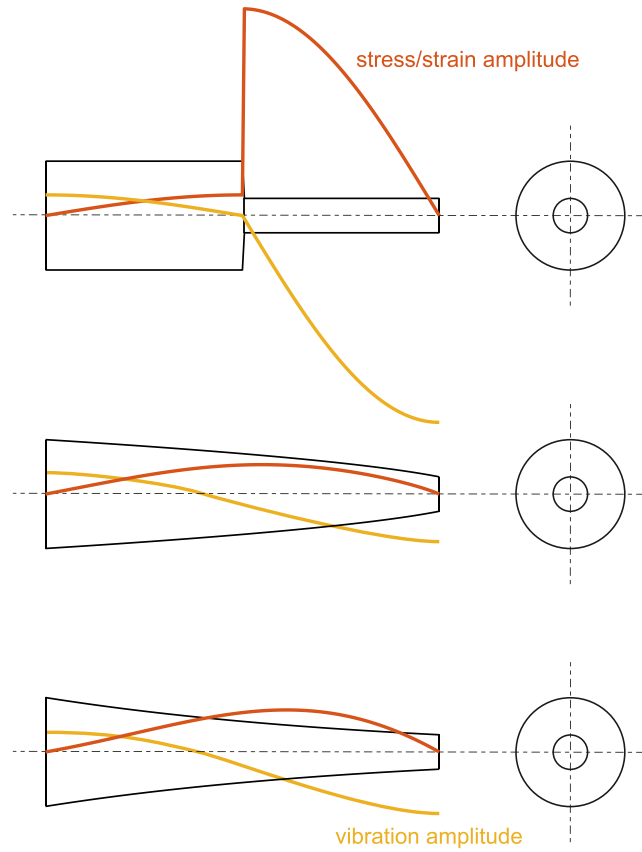


Fig. 4 Principle sketch of ultrasonic horns with their stress/strain and vibration amplitude distribution over length. Top: stepped horn, middle: linear cross-section shape function, bottom: exponential cross-section shape function.

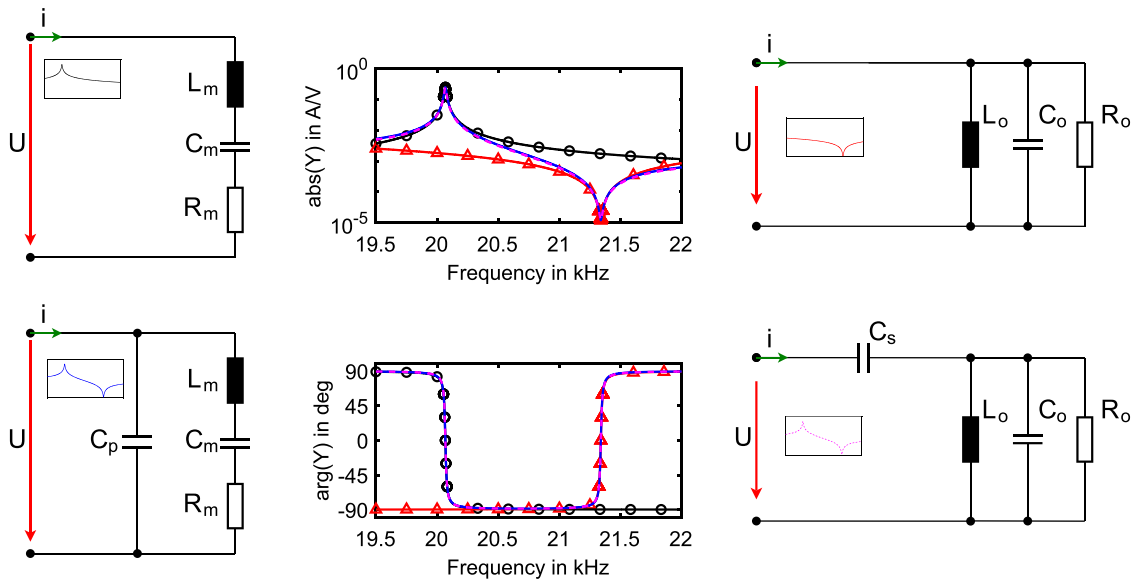


Fig. 5 Equivalent circuit models for power ultrasonic systems for resonance and anti-resonance operation.

analogies – see e. g. (Olson, 1943) – can be used to represent the full model in either electrical or mechanical domain. Most often the electrical domain is used.

The description of a very narrow frequency band around the resonance frequency can be done utilizing a RLC-serial branch, see Fig. 5, the admittance is given by

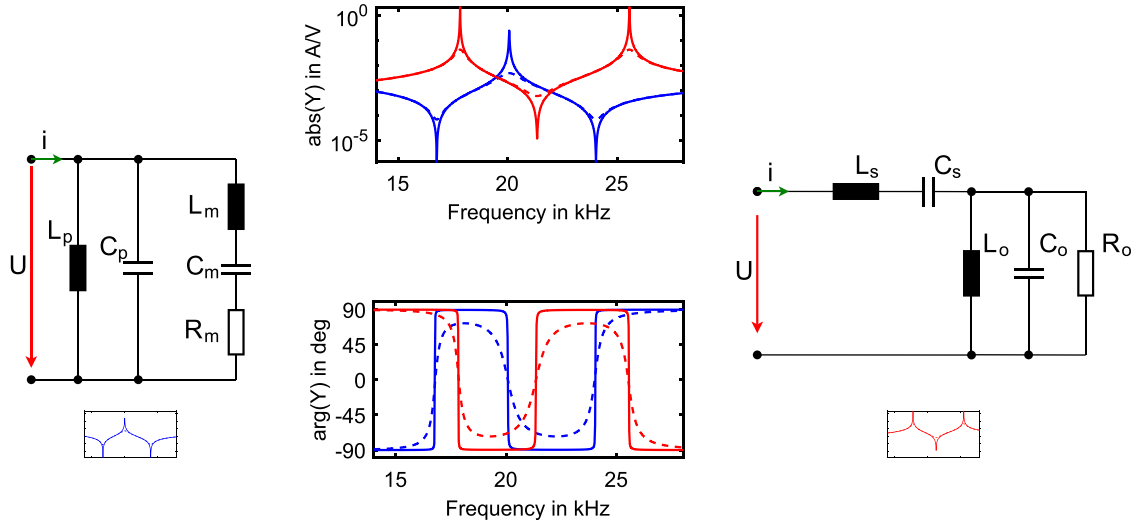


Fig. 6 Equivalent circuit models for power ultrasonic systems driven at resonance or anti-resonance with reactive power compensation. The dashed lines represent a case with higher damping e. g. due to the process load.

$$\underline{Y}_s = \frac{1}{j\Omega L_m + R_m + \frac{1}{j\Omega C_m}}, \quad (8)$$

with the angular excitation frequency Ω , the inductance L_m , the capacitance C_m , and the resistance R_m . The complex current amplitude in the RLC-branch is proportional to the complex velocity amplitude of the ultrasonic system. The addition of a parallel capacitance C_p extends the useful range over both resonance and anti-resonance.

$$\underline{Y}_e = \underline{Y}_s + j\Omega C_p \quad (9)$$

The so gained model is well known as Butterworth-van Dyke (BvD) model (Van Dyke, 1925). In the case, that the anti-resonance is of mayor interest, a parallel RLC circuit can be used, similar to the serial model it is valid in a close frequency regime. The corresponding admittance is

$$\underline{Y}_p = j\Omega C_o + \frac{1}{R_o + j\Omega L_o}. \quad (10)$$

In this case, the complex voltage amplitude over the RLC circuit is proportional to the complex velocity amplitude. This also can be extended to be valid in the complete resonance - anti-resonance frequency range. Here the addition of a serial capacitance C_s is needed. For this model typically the impedance

$$\underline{Z}_o = \frac{1}{\underline{Y}_o} = \frac{1}{\underline{Y}_p + j\Omega C_s} \quad (11)$$

is used instead of the admittance. All four models have the advantage, that they can be identified by electrical frequency response measurements – i.e., utilizing an impedance analyzer – only. The exemplary frequency response for a weak damped system in Fig. 5 shows that both models ($\underline{Y}_e$ and $\underline{Y}_o$) have a nearly identical response for a proper parameter identification.

As mentioned earlier, for operating medium or strong damped ultrasonic systems the compensation of the piezoelectric capacitance is desired to maintain phase zero (cp. Fig. 2). A short look on the equivalent models makes obvious, that a parallel inductance $L_p = \frac{1}{\omega_r^2 C_p}$ tuned to the angular resonance frequency ω_r allows to compensate C_p around the resonance. For anti-resonance a serial inductance $L_s = \frac{1}{\omega_a^2 C_s}$ tuned to the angular anti-resonance frequency ω_a has a similar effect for C_s . In each case the compensation is perfect at the designed frequency only. Fig. 6 shows the effect of a well matched capacitance compensation, for a weak and a high damped case. Here the additional damping, that, for example, is due to the process, can be modeled being part of R_m or R_o respectively.

Applications

Applications of power ultrasound are present in many different branches. To get an idea, why ultrasound can be used to initiate or enhance several processes, a short look on its peculiar features is advisable. Typically, mechanical vibrations with a displacement amplitude of up to 100 μm at 20 kHz can be generated. The maximum displacement amplitude drops with frequency, as dynamical stress in the mechanical structure rises with frequency and is limited by pre-stress of the ceramics and yield strength of the metal elements. While the resulting velocity amplitude of a sinusoidal vibration of 12.5 m/s is not technologically outstanding, the acceleration amplitude of more than 160.000 g is enormous! For sure, these free vibration amplitudes cannot be held up, when the vibrator is loaded, but nevertheless they remain unique compared to several other actuators: Coupled to a resonating air

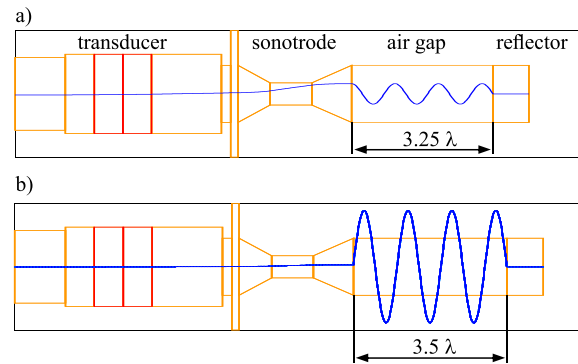


Fig. 7 Simulation results for longitudinal vibration amplitude in resonance over system length: a) for air-gap with length of 3.25λ , b) for air-gap tuned to 3.5λ .

field, sound pressure level might reach 186 dB, which is much more than that one generated by a starting airplane; in liquids, the fast varying pressure level produces streaming and cavitation resulting in micro-bubbles. Within mechanical contacts micro impact and friction manipulation by vibration superposition occur, which can be used for different material treatment or even transport mechanisms. The following paragraphs will report on some sample applications and systems therefor.

Airborne Power Ultrasound

Producing a standing wave acoustic field at ultrasonic frequency is easy at a first glance since the vibrating system should be merely influenced by air-load. But this is an erroneous belief as a resonantly tuned standing wave field causes other load characteristics than free radiation. By incorporating air and reflecting bodies within e. g. the half-lambda-synthesis mentioned above, vibration amplification and pressure increase are achieved, as shown in Fig. 7.

The ultrasonic acoustic pressure may be used to levitate objects (Lu *et al.*, 2021; Andrade *et al.*, 2018; Lierke and Holitzner, 2013), to atomize liquids (Gao *et al.*, 2021), or even produce local sound-events based on frequency modulation (Pompei, 2002). To achieve the highest sound pressure level the system depicted in Fig. 8 had been set up. It consists of a 20 kHz commercial standard bolted Langevin transducer, a booster (amplitude magnification factor 3,5), a custom made sonotrode (amplitude magnification factor 10) and a concave reflector, which is positioned to achieve a resonating standing wave field. The distance to the vibrating surface is adjusted considering the driving frequency (might drop during system heating!), imperfections of real sound propagation (not ideal plane waves, different path length to the reflector center and edges (Dunst *et al.*, 2019)) and finally non-linear characteristics of air due to high pressure level. Using this system, a sound pressure level of 182 dB was achieved and liquids with dynamic viscosity up to 100.000 mPas could be atomized into droplets.

Utilizing a tiny – micrometer range – air gap, a squeeze film can be generated, due to the non-linearity in air, the average pressure in the gap is higher than the ambient pressure. This can be used for contactless bearing applications (Salbu, 1964; Zhao, 2010). Compared to the magnetic levitation technology, the squeeze film levitation is inherently stable, as the levitation force increases with decreasing gap. The size of the gap is dynamically controllable (Mojrzisch and Twiefel, 2013).

Power Ultrasound in Liquids

Since the development of ultrasonic systems started with under water sonar, it might already have happened in that time that streaming and cavitation effects occurred (Noltingk and Neppiras, 1950). While cavitation unintendedly appears at rotating ship's propeller, the effect of generating and collapsing bubbles in fluids by local pressure variation due to ultrasonic vibration is welcome in many processes: widely spread is the application in cleaning baths, wherein surface pollutions are cracked and washed away by collapsing micro-bubbles and micro-jets (Crawford, 1963; Mason, 2016; Long *et al.*, 2019; Park *et al.*, 2021). If the ultrasound is directed to the surface of the liquid, capillary waves can lead to the formation of droplets, which is the base for the majority of ultrasonic nebulizers (Kooij *et al.*, 2019) reports on the size distribution of droplets generated by three different ultrasonic nebulizers). Many other applications got their own term: sonochemistry. The induced pressure variation, streaming and incredibly high pressure and temperature values (about 500 atmospheres and 5000°C) for short time instances initiate or at least enhance chemical reactions (Suslick, 1990; Yasui, 2021). The main benefit of applying ultrasound vibration in this field is, beside of making processes possible at all, the possibility to lower other demanding operating conditions like high temperature or pressure, or reaching higher yield and refined structures (e.g., at hydrothermal synthesis of piezoelectric material, (Isobe *et al.*, 2014)). Rather the same yields for some applications in food processing (Povey and Mason, 1998), waste treatment (Tyagi *et al.*, 2014), water cleaning (Ohrdes *et al.*, 2016), and even medical applications like phacoemulsification and liposuction (Miller *et al.*, 2012).

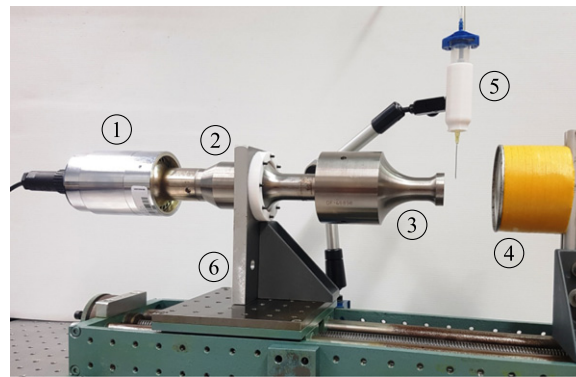


Fig. 8 Standing wave system for atomization of fluids with high viscosity: 1) transducer, 2) booster, 3) sonotrode, 4) reflector, 5) dosing unit, 6) linear stage.

Power Ultrasound in Solids

In metal-solids there are three main effects that occur due to ultrasound: the acoustoplastic effect, the enhanced diffusion, and the faster recrystallization.

The acoustoplastic effect (APE) consisting of stress superposition and acoustic softening, was first noted by [Blaha and Langenecker \(1955\)](#). The acoustic softening is attributed to the acoustic waves, which drive crystal defects away from their pinned position so that the yield stress of the material is lowered ([Blaha and Langenecker, 1959](#)). Since then, the acoustic softening has been extensively investigated for Al, Ti and Cu. The APE is important for numerous ultrasonic supported processes such as wire drawing, incremental sheet forming or ultrasonic metal welding.

When the strain amplitude exceeds a threshold value, ultrasound can dramatically enhance the diffusion process by introducing large amounts of vacancies ([Kulemin and Miskevich, 1971](#); [Abramov, 1994](#)). This has been substantially observed in ultrasonic welding processes ([Gunduz et al., 2005](#); [Panteli et al., 2012](#)). According to [Geissler et al. \(2011\)](#), under ultrasonic vibration, the activation energy of diffusion can be reduced by 48%.

Dynamic recrystallization is a common phenomenon occurring during ultrasonic welding ([Khatibi et al., 2012](#)), ultrasonic assisted metal forming ([Zhou et al., 2017](#)) and ultrasonic assisted additive manufacturing ([Todaro et al., 2020](#)). As the defect density is increased by ultrasound, more recrystallization nuclei can be formed so that the recrystallization process is greatly facilitated. This is especially prominent for high stacking fault energy (SFE) material, like Al, where submicron grains can be found ([Krzanowski and Murdeshwar, 1990](#)).

In plastics, due to viscoelastic material behavior and interface friction, a significant heating can be generated that can be high enough to melt thermoplastic materials. This allows the joining of plastic parts, many material combinations are possible ([Benatar, 2015](#)). To generate the heat at the right position, so-called energy directors are used. Utilizing these small, typically triangle shaped structures in the interface of the parts to join, the strain amplitude and therefore heat generation is maximized. The main advantages of ultrasonic plastics welding against other technologies are the high joining speed, the quality of the interconnection, absence of gluing layers and relatively low cost. Today, ultrasonic plastics welding is one of the most important power ultrasonic applications in industry.

Power Ultrasound at Interfaces

As stated above, ultrasonic atomization of liquids can be realized via ultrasound in air or liquids. As well, liquids can be dispersed from ultrasonically vibrating surfaces based on the high acceleration amplitudes achieved. The same yields for adhesive powders. They can be dispersed by surface vibration, mixed up in standing wave air field, and their stick behavior can be manipulated so that a keen transport gets possible ([Dunst et al., 2019](#)). Ultrasonic friction manipulation (or "reduction of effective friction"; ([Storck et al., 2002](#))) is used since a couple of decades in applications like wiredrawing ([Pohlman and Lehfeldt, 1966](#)) and cutting, wherein superimposed ultrasonic vibrations influence normal and/or tangential forces leading to unique features like reducing needed external forces and remaining clean tool surfaces. Often, these effects are enhanced by the acoustoplastic effect (APE, see above). Other applications profiting from friction manipulation and APE are drilling, milling ([Sarvi Hampa et al., 2015](#)), planing ([Willert et al., 2020](#)), lathing ([Sharma and Pandey, 2016](#)), grinding ([Abdullah et al., 2013](#)), polishing, and similar surface treatments together with or without conventional processing machines ([Kumar, 2013](#); [Singh and Singhal, 2016](#)).

As well, ultrasonic vibration can be used for joining processes of metals like wire bonding ([Long et al., 2017](#)) and metal welding, wherein additional to the acoustoplastic effect of the materials and abrasive cleaning of the surfaces ultrasound induced energy enhances the connection process. Ultrasound assisted sintering benefits from similar effects ([Haderler et al., 2021](#)). The intermittent or even continuous contact of vibrating bodies is also used in ultrasonic motors.

Future Directions

As shown in the above sections, the application of piezoelectric ultrasonic power transducers is multifold. While their basic design is rather simple, their efficient use in industrial applications often demands detailed investigation of the processes, thoroughly application oriented design of the transducers and ingenious control schemes. This becomes possible by implementing models for the nonlinear behavior of the systems, might they be caused by the nonlinear material characteristics of the piezoelectric elements, by contact mechanics, or non-linearities in the processes. Of course, this raises computing effort, but with enhanced computing technologies and co-simulation of different standard software, many new insights in processes and simulation based optimization get possible (Schemmel *et al.*, 2021).

The urgent need for more information on processes motivates work to utilize the mechanical-electrical conversion capability of the piezoelectric elements simultaneously to its actuation capability. Hofmann and Twiefel (2017) describe an approach utilizing the measured electrical input (voltage and current) and a transfer matrix model to estimate the mechanical boundaries at the process interface (force and velocity). Also information on the process can be gained using the data at the electrical port, this has been demonstrated for the estimation of the cavitation activity in (Saalbach *et al.*, 2019). This concept has the potential for sensor-less (only the driving transducer) process monitoring and will enable numerous new functions.

Another topic of the future is the development of lead free power transducers being driven by legal restrictions such as (RoHS 2). There are several materials already commercially available that could replace PZT in some low power applications, but for building high power transducers efficient lead free materials are missing yet. As well, high power characteristics of piezoelectric materials are not fully investigated. (EN 50324–3) indicates how to measure strain dependent material characteristics, but this covers the complex thermo-electro-mechanical coupling behavior of pre-stressed high power transducers only in part. Therefore the development of new material models and computing algorithms remain attractive tasks for future research.

Closing Remarks

Power ultrasound is mature technology, that has proven its applicability in various fields. This includes industrial, automotive, medical and chemical applications. Nowadays, it is estimated that everybody in industrialized countries is in daily contact to products made with the help of ultrasound. Nevertheless, the ultrasonic technologies remain widely invisible for the customer. However, the ongoing research shows that the full potential of high power ultrasound is not used yet. Especially, delivering the energy directly into the process area has a large potential for more efficient and ecologically sustainable production processes.

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Ferroelectric Devices

Kenji Uchino, Electrical Engineering, The Penn State University, University Park, PA, United States

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Abstract

Ferroelectrics can be applied diversely to high-permittivity dielectrics, ferroelectric memories, pyroelectric sensors, piezoelectric devices, electrooptic devices and PTCR (positive temperature coefficient of resistivity) components. This article is authored to provide the fundamental background of ferroelectrics, practical materials, then, operation principles of the above applied devices, followed by the future perspectives. The article covers particularly (1) crystal structure and ferroelectricity, (2) origin of spontaneous polarization, (3) electrooptic phenomena, (4) origin of field induced strain, (5) ferroelectric phenomenology, (6) ferroelectric/ piezoelectric materials, and finally (7) ferroelectric device applications. This article is primarily based on the author's textbook, "Ferroelectric Devices 2nd Edition".

Key Points

- crystal structure and ferroelectricity.
- origin of spontaneous polarization.
- electrooptic phenomena.
- origin of field induced strain.
- ferroelectric phenomenology.
- ferroelectric/ piezoelectric materials.
- ferroelectric device applications.

Introduction

Ferroelectrics can be applied diversely to high-permittivity dielectrics, ferroelectric memories, pyroelectric sensors, piezoelectric devices, electrooptic devices and PTCR (positive temperature coefficient of resistivity) components. This article is authored to provide the fundamental background of ferroelectrics, practical materials, then, operation principles of the above applied devices, followed by the future perspectives. The article covers particularly (1) crystal structure and ferroelectricity, (2) origin of spontaneous polarization, (3) electrooptic phenomena, (4) origin of field induced strain, (5) ferroelectric phenomenology, (6) ferroelectric/ piezoelectric materials, and finally (7) ferroelectric device applications. This article is primarily based on the author's textbook, "Ferroelectric Devices 2nd Edition" (Uchino, 2009).

Crystal Structure and Ferroelectricity

In so-called "dielectric materials", the constituent atoms are considered to be ionized to a certain degree and are either positively or negatively charged. In such ionic crystals (covalent in polymers), when an electric field is applied, cations are attracted to the cathode and anions to the anode due to electrostatic interaction. The electron clouds also deform, causing electric dipoles. This phenomenon is known as "electric polarization" of the dielectric, and the polarization is expressed quantitatively as the sum of the "electric dipoles" per unit volume [C/m²]. Fig. 1 shows schematically the origin of the electric polarization. There are three primary contributions: "electronic", "ionic" and "dipole reorientation-related". These three mechanisms contribute to the overall polarization of the material depends on the frequency of the applied electric field. Electronic polarization can follow alternating fields with frequencies up to THz-PHz (10¹² – 10¹⁵ cycle/sec, higher than visible light wave), while ionic polarization responds up to GHz-THz (10⁹ – 10¹² cycle/sec, microwave region). Thus, you should understand that a famous relation between the relative permittivity ϵ_r and refractive index n :

$$\epsilon_r = n^2 \quad (1)$$

is valid only when the applied electric field has a frequency on the order of THz or higher. Permanent dipole reorientation can follow only up to MHz-GHz (10⁶ – 10⁹ cycle/sec). This is why ferroelectric materials with permanent dipoles cannot be used for microwave dielectric materials; their permittivity is typically high at low frequencies (kHz), but decreases significantly with increasing applied electric field frequency. Frequency dependence of the total polarizability (or permittivity) is depicted in Fig. 2.

Compared with air-filled capacitors, dielectric capacitors can store more electric charge due to the dielectric polarization P , as shown in Fig. 3. The physical quantity corresponding to the stored electric charge per unit area is called the "electric displacement" D , and is related to the electric field E by the following expression:

$$D = \epsilon_0 E + P = \epsilon_0 \epsilon_r E \quad (2)$$

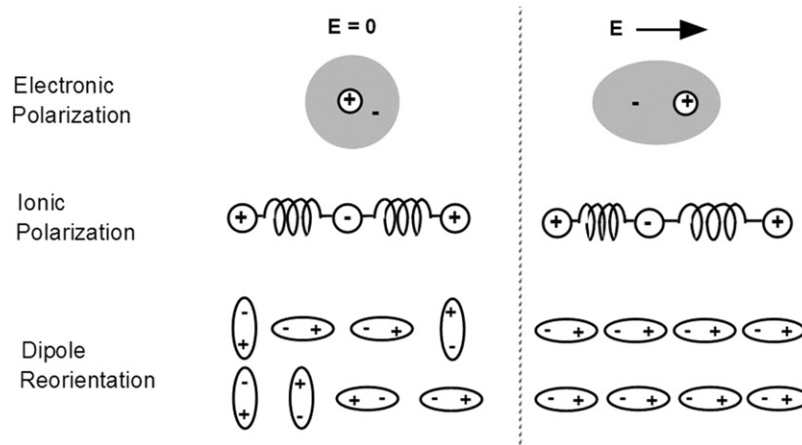


Fig. 1 Microscopic origins of the electric polarization.

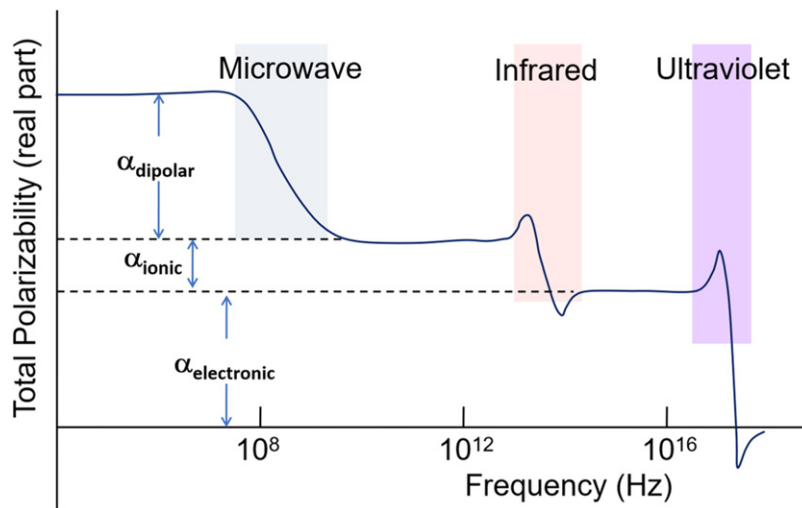


Fig. 2 Frequency dependence of the polarizability (or permittivity).

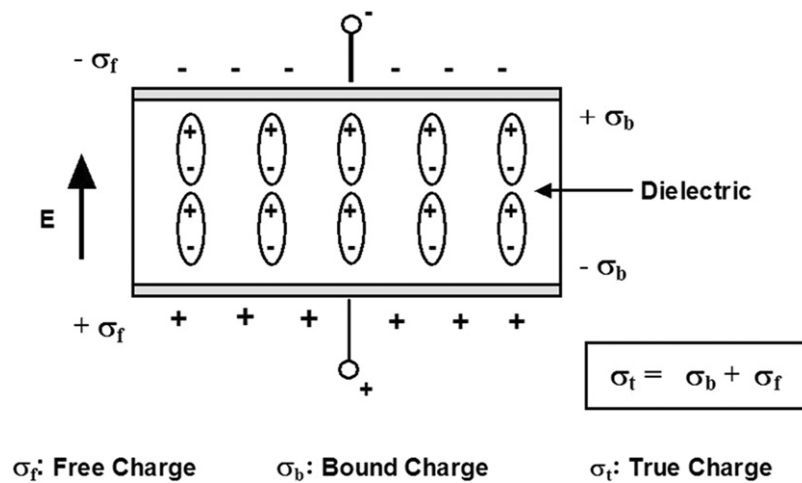


Fig. 3 Charge accumulation in a dielectric capacitor.

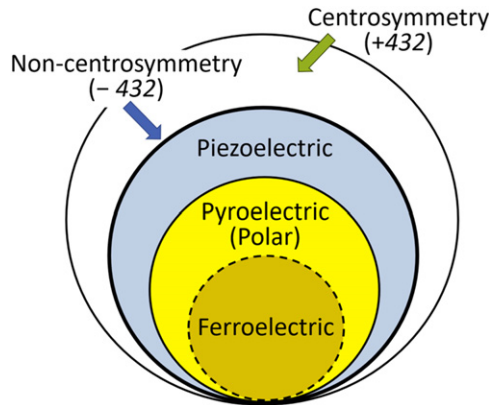


Fig. 4 Classification of dielectrics according to crystal centro-symmetry and polarity.

Here, ϵ_0 is the vacuum permittivity ($= 8.854 \times 10^{-12}$ F/m), ϵ_r is the material's relative permittivity (also simply called permittivity or dielectric constant, and in general is a tensor parameter). Because of the induced polarization P , a couple of orders of magnitude larger free charge can be stored in an electrode dielectric capacitor, as shown in Fig. 3.

Depending on the crystal structure, the centers of the positive and negative charges may not coincide even without the application of an external electric field. Such crystals are said to possess a “spontaneous polarization” (or “pyroelectric”). When the spontaneous polarization direction of the dielectric can be reversed by an electric field, it is called “ferroelectric”.

Not every dielectric is a ferroelectric. Crystals can be classified into 32 point-groups according to their crystallographic symmetry, and these point groups can be divided into two classes, one with a center of symmetry and the other without. There are 21 point-groups which do not have a center of symmetry, as shown in Fig. 4. In crystals belonging to 20 of these point groups [point group (432) being the sole exception], positive and negative charges are generated on the crystal surfaces when stresses are applied (i.e., “direct piezoelectric effect”), which are known as “piezoelectrics”. 10 point-groups among piezoelectrics possess spontaneous polarization (i.e., polar, or pyroelectric). “Pyroelectricity” is the phenomenon whereby, as the temperature of the crystal is changed, electric charges corresponding to the change of the spontaneous polarization appear on the surface of the crystal. Among the pyroelectric crystals, those whose spontaneous polarization direction can be reversed by an electric field (not exceeding the breakdown limit of the crystal) are called “ferroelectrics”. Thus, there is some experimental ambiguity in this definition; in establishing “ferroelectricity”, it is necessary to apply an electric field to a pyroelectric material and experimentally ascertain the polarization reversal.

Origin of Spontaneous Polarization

Soft Phonon Mode

Why is it that crystals which, from a consideration of elastic energy, should be stable by being non-polar, still experience the shifting of cations and anions and become spontaneously polarized? The reason is briefly explained below. For simplicity, let us assume that dipole moments result from the displacement of one type of ion A (electric charge $+q$) relative to the crystal lattice. Consider the case in which the polarization is caused by all the A ions being displaced equally in a lattice cooperatively. This kind of ionic displacement can be expected through “crystal lattice vibrations” at a finite temperature. Fig. 5 shows some of possible eigen lattice vibrations in a perovskite-like crystal. (a) shows an initial cubic (symmetrical) structure, (b) is a symmetrically elongated one (i.e., no polarization is generated), (c) has coherently shifted center positive cations (i.e., the rightward polarization), and (d) exhibits an antipolarized zig-zag shift of the center cations (i.e., no net polarization as a whole). If one particular lattice vibration mode lowers the crystal energy, the ions will shift and stabilize the crystal structure so as to minimize the energy. Starting from the original cubic structure (a), if (b) is stabilized, only oxygen octahedra are distorted without generating dipole moments (acoustic mode). On the other hand, when (c) or (d) is stabilized, dipole moments are generated (optical mode). The final stabilized states (c) and (d) correspond to “ferroelectric” and “antiferroelectric” states, respectively. If this particular mode becomes stabilized, with decreasing temperature, the vibration mode frequency decreases (i.e., “soft phonon mode”), and finally at a certain phase transition temperature this frequency becomes zero.

Local Electric Field and Dipole Coupling Energy

What is the microscopic origin of the spontaneous shift of the ions? At any individual A ion site, there exists a “local electric field” from the surrounding polarization P , even if there is no external field. The concept of the local field is shown schematically in Fig. 6. It can be shown that:

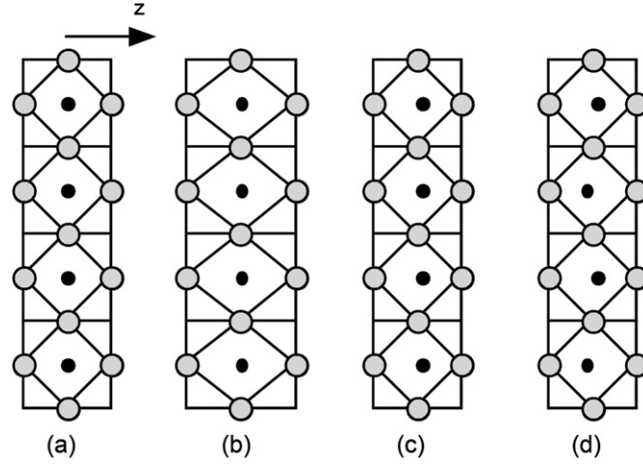


Fig. 5 Some possible eigen lattice vibration modes in a perovskite crystal.

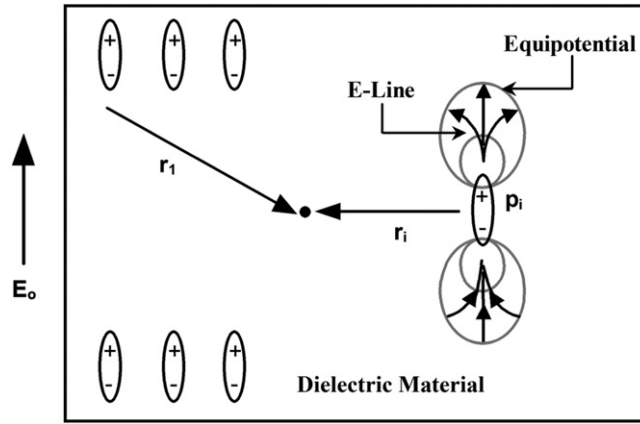


Fig. 6 Concept of the local field. E^{loc} is given by $E^{loc} = E_0 + \sum_i [3(\mathbf{p}_i \cdot \mathbf{r}_i) \mathbf{r}_i - r_i^2 \mathbf{p}_i] / 4\pi\epsilon_0 r_i^5$.

$$E^{loc} = E_0 + \sum_i [3(\mathbf{p}_i \cdot \mathbf{r}_i) \mathbf{r}_i - r_i^2 \mathbf{p}_i] / 4\pi\epsilon_0 r_i^5 = (\gamma/3\epsilon_0) \mathbf{P}. \quad (3)$$

This local field is the driving force for the ion shift. Here γ is called the “Lorentz factor”, a sort of “feedback amplification factor”. For an isotropic cubic system, it is known that $\gamma = 1$ (Kittel, 1986) and γ becomes large for a certain ferroelectric structure. ϵ_0 is the permittivity of vacuum and is equal to 8.854×10^{-12} F/m. If the “ionic polarizability” of ion A is μ , then the “dipole moment” of the unit cell of this crystal is:

$$\mu = (\alpha\gamma/3\epsilon_0) \mathbf{P} \quad (4)$$

The energy of this dipole moment (dipole-dipole coupling) is

$$w_{dip} = -\mu \cdot E^{loc} = -(\alpha\gamma^2/9\epsilon_0^2) \mathbf{P}^2 \quad (5)$$

Defining N to be the number of atoms per unit volume:

$$W_{dip} = Nw_{dip} = -(N\alpha\gamma^2/9\epsilon_0^2) \mathbf{P}^2 \quad (6)$$

This “dipole-dipole coupling energy” gives the promotion of the spontaneous ionic shift. On the other hand, when the A ions are displaced from their nonpolar equilibrium positions, the “elastic energy” is increased, which suppresses the ionic shift. If the displacement is $\mathbf{u}$, and the force constants k and k' , then the increase of the elastic energy per unit volume can be expressed as:

$$W_{elas} = N \left[(k/2) \mathbf{u}^2 + (k'/4) \mathbf{u}^4 \right] \quad (7)$$

Here, $k' (> 0)$ is the higher-order force constant. It should be noted that in pyroelectrics (i.e., polar status), k' plays an important role in determining the magnitude of the dipole moment. Rewriting Eq. (7) with:

$$\mathbf{P} = Nq\mathbf{u}, \quad (8)$$

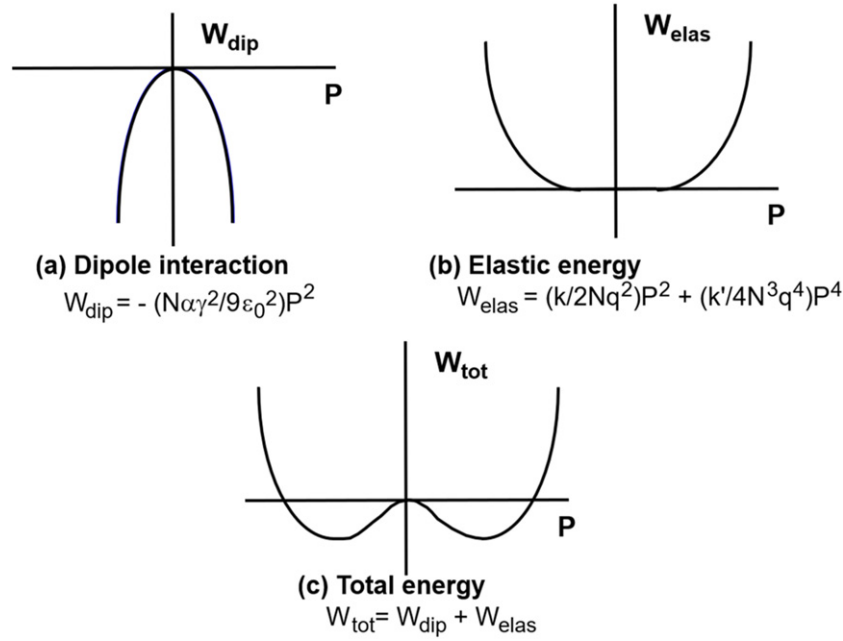


Fig. 7 Energy explanation of the origin of spontaneous polarization.

where q is the electric charge, and combining with Eq. (6), the total energy can be expressed as follows (see Fig. 7):

$$W_{\text{tot}} = W_{\text{dip}} + W_{\text{elas}} = \left[\left(\frac{k}{2Nq^2} \right) - \left(\frac{N\alpha\gamma^2}{9\epsilon_0^2} \right) \right] P^2 + \left[\frac{k'}{4N^3q^4} \right] P^4 \quad (9)$$

From this, one can see that if the coefficient of the harmonic (k) term of the elastic energy is equal to or greater than the coefficient of the dipole-dipole coupling, then $P = 0$; the A ions are stable and remain at the non-polar equilibrium positions. Otherwise, a shift from the equilibrium position ($P^2 = [(4N\alpha\gamma^2/9\epsilon_0^2) - (2k/Nq^2)] / [k'/N^3q^4]$) is stable. Spontaneous polarization can occur more easily in perovskite type crystal structure (e.g., barium titanate) due to a higher value of Lorenz factor γ ($= 10$) (Kinase *et al.*, 1969) than found for other crystal structures. Note also that the polarizability is changed with temperature, leading to the phase transition. Suppose that the ionic polarizability of ion A, α , increases with decreasing temperature, even if $[(k/2Nq^2) - (N\alpha\gamma^2/9\epsilon_0^2)] > 0$ (paraelectric!) at a high temperature, this value may become negative with decreasing temperature, leading to a ferroelectric phase transition. Considering the first approximation, a linear relation of the α with temperature, that is, the well-known “Curie-Weiss law”:

$$\left[\left(\frac{k}{2Nq^2} \right) - \left(\frac{N\alpha\gamma^2}{9\epsilon_0^2} \right) \right] = (T - T_0)/\epsilon_0 C \quad (10)$$

can be derived.

Electrooptic Phenomena

Since light is an alternating electromagnetic wave with electric and magnetic field vibration directions mutually almost-perpendicular to one another, the electric field induces an electric polarization in a dielectric crystal and the light itself is influenced by the crystal. The alternating frequency of the light is so high (PHz = 10^{15} Hz) that only the “electronic polarization” can follow the electric field change (see Fig. 2), and the relative permittivity ϵ_r of an optically transparent crystal is small, not exceeding 10. As introduced already, the relative permittivity ϵ_r at this high frequency is related to the refractive index n by the following equation: $\epsilon_r = n^2$.

Electrooptic Effect

When an external electric field is applied to the crystal, ionic displacement is induced, deforming the shape of the electron cloud, and consequently the “refractive index” n is changed. The refractive index is related with the electron density in a material directly. This phenomenon is called the “electrooptic effect” (Uchino, 2009). Generally, the refractive index is treated as a symmetrical second-rank tensor quantity (similar to the permittivity) and is represented geometrically by the “optical indicatrix” which is described by

$$\frac{x^2}{n_1^2} + \frac{y^2}{n_2^2} + \frac{z^2}{n_3^2} = 1, \quad (11)$$

where n_1 , n_2 and n_3 are the principal refractive indices. With the application of an electric field, the change in refractive index is given by a Taylor/Maclaurin expansion expression of $(1/n_i^2)$ in terms of E :

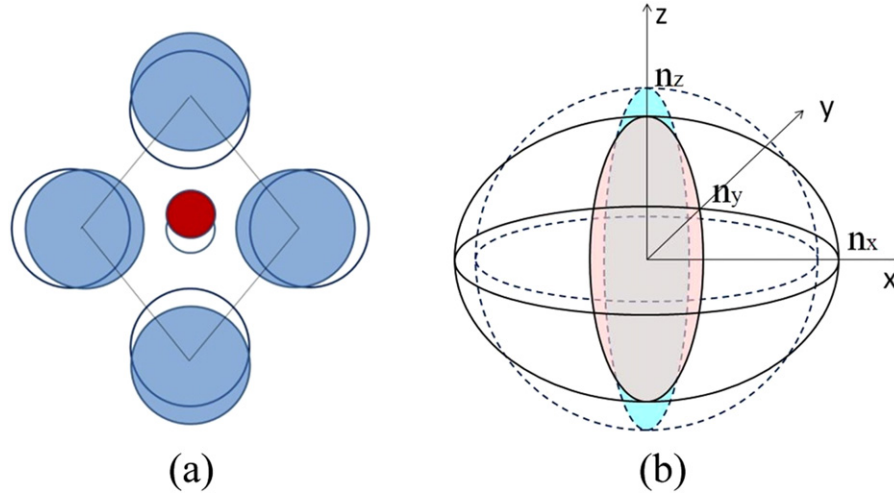


Fig. 8 (a) Perovskite unit cell change with electric field. (b) Corresponding refractive indicatrix change of a cubic crystal with electric field (Kerr effect). An original sphere becomes a doughnut shape.

$$1/n_{ij}^2(E) - 1/n_{ij}^2(0) = \sum r_{ijk}E_k + \sum R_{ijkl}E_kE_l. \quad (12)$$

Here $n(E)$ and $n(0)$ ($= n_0$) are the refractive indices at E and zero field, respectively, and r_{ijk} is the primary electrooptic coefficient ("Pockels effect") and R_{ijkl} is the secondary coefficient ("Kerr effect"). Remember that the Maclaurin expansion is not based on n_{ij} , but on $1/n_{ij}^2$ (originated from the expansion of the inverse permittivity κ_{ij}).

Considering the paraelectric phase of a perovskite crystal ($m3m$) as an example, the Kerr coefficients are represented in the following matrix:

$$\begin{pmatrix} R_{11} & R_{12} & R_{12} & 0 & 0 & 0 \\ R_{12} & R_{11} & R_{12} & 0 & 0 & 0 \\ R_{12} & R_{12} & R_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & R_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & R_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & R_{44} \end{pmatrix}$$

so that the "refractive indicatrix" under an electric field applied along the z direction is expressed as:

$$\frac{x^2 + y^2}{n_0^2 \left[1 - \left(\frac{n_0^2}{2} \right) R_{12} E_z^2 \right]^2} + \frac{z^2}{n_0^2 \left[1 - \left(\frac{n_0^2}{2} \right) R_{11} E_z^2 \right]^2} = 1 \quad (13)$$

The refractive index change under an external electric field is explained intuitively in Fig. 8(a). When an electric field E_z is applied to a cubic perovskite crystal (for example), the crystal is elongated along the z -axis and contracted perpendicularly along both the x and y axes via the electrostrictive effect (see Section "Origin of Field Induced Strain"). Consequently, the material's density or compactness will be decreased along the z -axis and densified along the x and y axes, leading to a decrease in the refractive index n_z and an increase of the indices n_x and n_y , as illustrated in Fig. 8(b) (The sphere becomes a doughnut-shape). Note that the refractive index is proportional to the electron density or ion compactness along the polarized light electric field direction which is perpendicular to the light propagation direction. Taking into account the above description, R_{11} and R_{12} in Eq. (13) should be positive and negative, respectively, directly correlated with the electrostrictive coefficients M_{ij} . Similar crystal cell elongation to Fig. 8(a) under positive stress applied along the z -axis exhibits similar doughnut-shape indicatrix change, which is called "elasto-optic effect".

Principle of Optical Shutter

When light beam with wavelength λ is transmitted in a cubic crystal ($m3m$) along the y direction through a "polarizer" arranged 45° cant from the electric field z direction, as shown in Fig. 9, the light beam becomes composed of "extraordinary" and "ordinary rays". The extraordinary ray (polarized along the z direction) experiences the refractive index $n_e = n_0 \left[1 - \left(\frac{n_0^2}{2} \right) R_{11} E_z^2 \right]$, leading to a little slower light speed in the crystal given by c/n_e ; while the ordinary ray (polarized along the x direction) experiences the refractive index $n_o = n_0 \left[1 - \left(\frac{n_0^2}{2} \right) R_{12} E_z^2 \right]$, leading to a little faster light speed in the crystal given by c/n_o . Thus, after passing through the crystal distance L , there exists a phase retardation Γ_y between the ordinary (polarized along the x orientation) and extraordinary waves (polarized along the electric field z orientation), which is calculated as

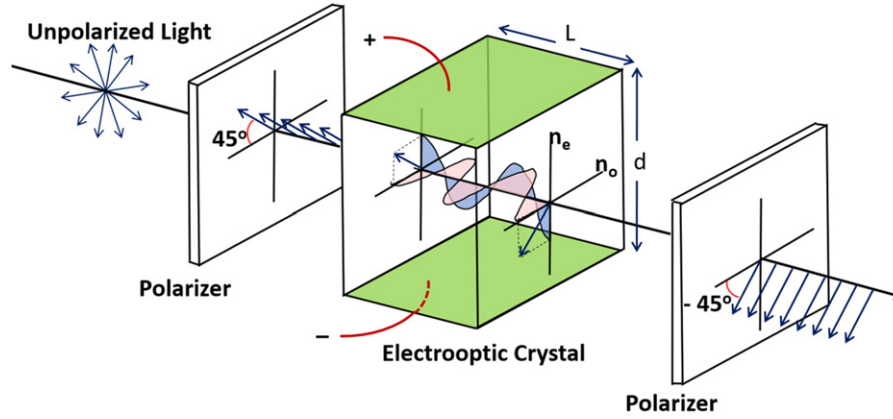


Fig. 9 Optical phase retardation through an electrooptic crystal between extraordinary and ordinary rays. Notice the crossed polarizer configuration.

$$\Gamma_y = (2\pi/\lambda)(n_o^3/2)(R_{11} - R_{12})L(V_z/d)^2, \quad (14)$$

where λ is the light wavelength, d and L are the electrode gap and “optical path length”, respectively. Placing another polarizer arranged at -45° angle with respect to the z -axis (i.e., so-called “crossed polarizer” configuration), the output light intensity is expressed as a function of the retardation Γ_y , which is modulated by the applied voltage (Eq. (14)):

$$I = I_0 \sin^2(\Gamma_y/2) = (1/2)I_0(1 - \cos\Gamma_y). \quad (15)$$

Fig. 10 plots the variation in the light intensity of a “Kerr-effect electrooptic shutter” with applied voltage, under a polarizer and an analyzer crossed-nicols. The sinusoidal intensity modulation period shrinks gradually with voltage, because the retardation Γ_y is proportional to the square of the applied voltage (i.e., “secondary electrooptic effect”). This is the principle behind the operation of a light shutter/valve, and the voltage required for the first intensity maximum (i.e., $\Gamma_y = \pi$) is an important characteristic called the “half-wave voltage”:

$$V_{z,\lambda/2} = d\sqrt{\lambda_0/Ln_0^3(R_{11} - R_{12})} \quad (16)$$

Origin of Field Induced Strain

Solids, especially ceramics (inorganic materials), are relatively hard mechanically, but still expand or contract depending on the change of the input parameters. The “strain” (defined as the “displacement” ΔL /initial length L) caused by temperature change or stress is known as “thermal expansion” or “elastic deformation”, respectively. In insulating materials, the application of an electric field can also cause deformation, which is called “electric field induced strain” (Similarly, a magnetic field on a particular magnetic material generates strain, called “magnetostriction”, which is excluded in this manuscript). There are three kinds: “piezoelectric strain”, “electrostriction”, and the “domain-reorientation-based strain”. We consider the microscopic origin in this section.

Piezoelectric Strain

The “converse piezoelectric effect” is defined as a primary electromechanical coupling effect, that is, the strain is proportional to the electric field; while “electrostriction” is a secondary coupling in which the strain is proportional to the square of the electric field. Thus, they are distinguished. However, the piezoelectricity of a ferroelectric, which has a centro-symmetric prototype phase at an elevated temperature, is considered to originate from the “electrostrictive coupling”, hence these two effects are related, as phenomenologically explained in the next section.

Why a strain is induced by an electric field is explained herewith (Uchino and Nomura, 1983). For simplicity, let us consider a diatomic ionic crystal such as NaCl. **Fig. 11(a)** and **(b)** show a 1D “rigid-ion spring model” of the crystal lattice. The springs represent equivalently the cohesive force resulting from the electrostatic Coulomb energy and the quantum mechanical repulsive energy. **Fig. 11(b)** shows the centro-symmetric case, whereas **Fig. 11(a)** shows the more general non-centrosymmetric case. In **(b)**, the springs joining the ions are all the same, whereas in **(a)**, the springs joining the ions are different for the longer and shorter ionic distances, in other words, hard and soft springs existing alternately are important. Next, consider the state of the crystal lattice **(a)** under an applied electric field. The cations are drawn in the direction of the electric field and the anions in the opposite direction, leading to the relative change in the inter-ionic distance. Depending on the direction of the electric field, the soft spring expands or contracts more than the contraction or expansion of the hard spring in order to maintain the same atomic interaction forces, causing a strain x (a unit cell length change) in proportion to the electric field E . This is the “converse piezoelectric effect”. When expressed as

$$x = dE, \quad (17)$$

the proportionality constant d is called the “piezoelectric constant”.

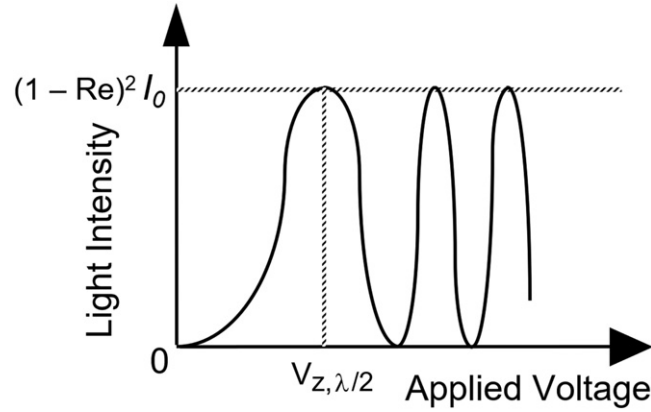


Fig. 10 Variation in the light intensity of a Kerr-effect electrooptic shutter with applied voltage.

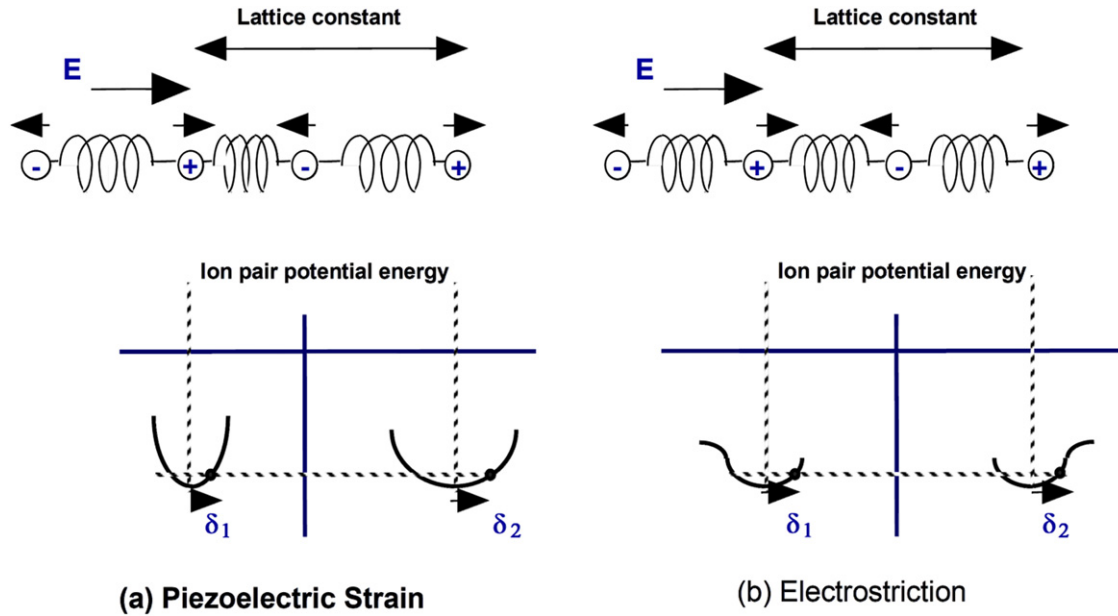


Fig. 11 Microscopic explanation of the piezoelectric strain (a), and electrostriction (b).

Electrostriction

On the other hand, in **Fig. 11(b)**, the amounts of extension and contraction of the spring are nearly the same, thus the distance between the two cations (lattice parameter) remains almost the same, hence, there is no strain. However, more precisely, ions are not connected by such idealized springs (called “harmonic springs” in which force (F) = spring constant (k) $\times$ displacement (Δ) holds). In most cases, the springs possess “anharmonicity” ($F = k_1\Delta - k_2\Delta^2$), that is, they are somewhat easy to extend but hard to contract. Such subtle difference in the displacement causes a change in the lattice parameter, producing a strain which is independent of the direction of the applied electric field ($+E$ or $-E$), and hence is an even-function of the electric field. This is called the “electrostrictive effect”, and can be expressed as

$$x = ME^2, \quad (18)$$

where M is the “electrostrictive coefficient”.

Note that the 1D asymmetric crystal pictured in **Fig. 11(a)** also possesses a spontaneous bias of electrical charge, or a “spontaneous dipole moment”. The total dipole moment per unit volume is called the “spontaneous polarization”. When a large reverse bias electric field is applied to a crystal that has a positively aligned spontaneous polarization, another polarization status is formed which is another stable crystal state in which the relative positions of the ions are reversed. In terms of an untwinned single crystal, this is equivalent to rotating the crystal 180° about an axis perpendicular to its polar axis. This transition, referred to as “polarization reversal”, also causes a remarkable change in strain. This particular class of substances is referred to as “ferroelectrics”, as mentioned in Section “Crystal Structure and Ferroelectricity”.

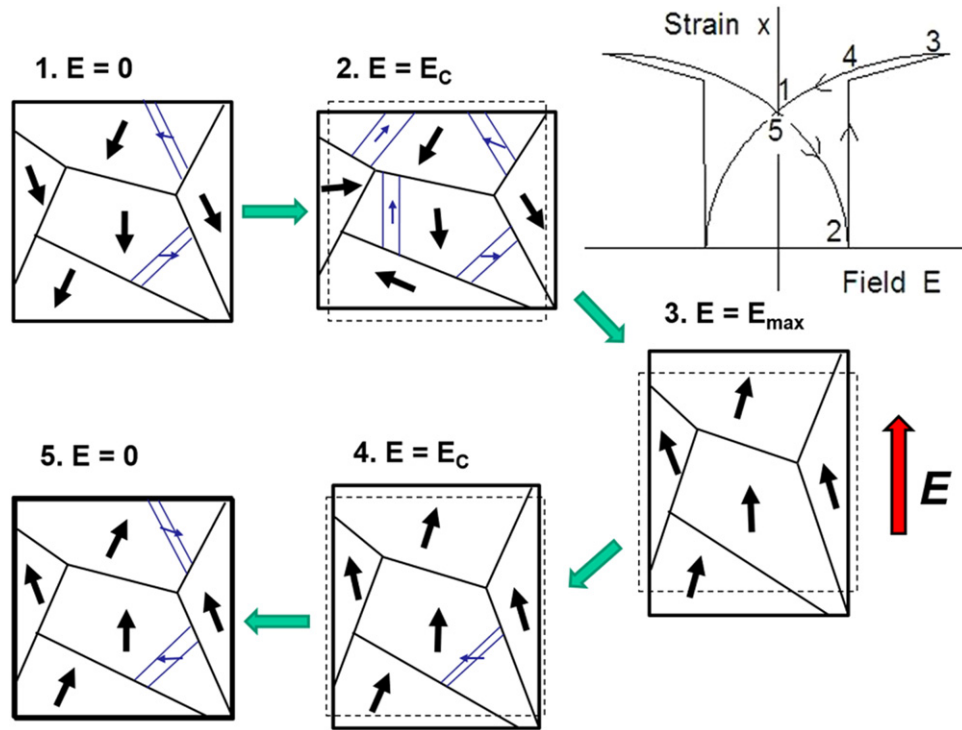


Fig. 12 Domain structure change with the external electric field in polycrystalline ferroelectrics.

Polarization-Reorientation Related Strain

Schematic “polarization reorientation” process or “poling process” in a polycrystalline ferroelectric specimen such as lead zirconate titanate (PZT) is illustrated in Fig. 12. First, the polycrystal is composed of many small single crystals (each is called “grain”) with random crystal orientations. Thus, the complete alignment of the polarization is impossible. Further, due to this crystallographic mis-orientation, some residual stress exists in the specimen, which promotes multi-domain status even under a high electric field. We start from the initially “negatively poled” status “1”. You can notice some residual domains in each grain. With increasing the electric field up to the “coercive” field E_c “2” (where the free energy at $-P_s$ reaches zero), the largest number of various domains come up and the total polarization becomes almost zero. When we further increase the field “3”, the domain rapidly disappears to become close to mono-domain state in each grain. The slope of the strain vs. electric field around “3” corresponds to the intrinsic piezoelectric constant. Now if we decrease the field down to the coercive field “4”, we may start to observe some domain generation in grains, then finally at zero field “5”, we observe similar domains in each grain as in the state “1”, though the polarization directions are opposite to the state “1”. We call this state “positively poled”. Generally, what actually observed as a field-induced strain is a complicated combination of the above three basic effects: (1) piezoelectric, (2) electrostriction, and (3) domain-reorientation-related (hysteretic) strain.

Ferroelectric Phenomenology

Let us now consider the phenomenological approach to a ferroelectric, where the free energy is expanded in the Maclaurin/Taylor series in terms of externally-controlling parameters (“intensive parameters”) and/or “order parameters”. “Order parameter” can distinguish two different phases; for example, polarization P distinguishes paraelectric ($P = 0$) and ferroelectric phases ($P \neq 0$).

Linear Coupling in Ferroelectrics

We consider a practical formula of the Gibbs free energy $G(T, X, E)$ for the case of small value change in temperature $\theta = T - T_R$ (room temperature), external X and E (1D case). If the change of parameters is small, we may adopt the three-parameter Taylor expansion approximation up to second derivatives in order to discuss just the linear relationships, based on the description by Mitsui *et al.* (1969).

$$G(T, X, E) = G_0 + \left(\frac{\partial G}{\partial T}\right)\theta + \left(\frac{\partial G}{\partial X}\right)X + \left(\frac{\partial G}{\partial E}\right)E$$

$$\begin{aligned}
& + \frac{1}{2} \left(\frac{\partial^2 G}{\partial T^2} \right) \theta^2 + \frac{1}{2} \left(\frac{\partial^2 G}{\partial X^2} \right) X^2 + \frac{1}{2} \left(\frac{\partial^2 G}{\partial E^2} \right) E^2 \\
& + \left(\frac{\partial^2 G}{\partial T \partial X} \right) \theta X + \left(\frac{\partial^2 G}{\partial T \partial E} \right) \theta E + \left(\frac{\partial^2 G}{\partial X \partial E} \right) XE
\end{aligned} \quad (19)$$

Taking into account $dG = -SdT - x dX - D dE$, we obtain first the relations, $\left(\frac{\partial G}{\partial T} \right)_{\theta, X, E=0} = -S_0$, $\left(\frac{\partial G}{\partial X} \right)_{\theta, X, E=0} = -x_0$ and $\left(\frac{\partial G}{\partial E} \right)_{\theta, X, E=0} = -D_0$. Since S_0 is the entropy density at $\theta, X, E = 0$, we take this as the “origin” value and set it $S_0 = 0$. The values x_0 and D_0 ($\approx P_0$) are considered to be spontaneous strain and spontaneous polarization in the ferroelectric phase of this material, thus we set them as new “origins” in the discussion merely in the ferroelectric phase. Now, Eq. (19) can be transformed as

$$S = - \left(\frac{\partial G}{\partial T} \right) = - \left(\frac{\partial^2 G}{\partial T^2} \right) \theta - \left(\frac{\partial^2 G}{\partial T \partial X} \right) X - \left(\frac{\partial^2 G}{\partial T \partial E} \right) E \quad (20a)$$

$$x = - \left(\frac{\partial G}{\partial X} \right) = - \left(\frac{\partial^2 G}{\partial T \partial X} \right) \theta - \left(\frac{\partial^2 G}{\partial X^2} \right) X - \left(\frac{\partial^2 G}{\partial X \partial E} \right) E \quad (20b)$$

$$D = - \left(\frac{\partial G}{\partial E} \right) = - \left(\frac{\partial^2 G}{\partial T \partial E} \right) \theta - \left(\frac{\partial^2 G}{\partial X \partial E} \right) X - \left(\frac{\partial^2 G}{\partial E^2} \right) E \quad (20c)$$

Based on the above linear relationships, we derive several types of “constitutive equations” in the following sections.

Adiabatic process 1 – Piezothermal effect

We consider the “adiabatic process”; that is, the specimen is isolated from the external heat source, and temperature may be changed during the energy conversion process by the external input. When the electric field is constant, $E = 0$ in Eqs. (20a) and (20b), we can obtain the following equations:

$$S = - \left(\frac{\partial^2 G}{\partial T^2} \right) \theta - \left(\frac{\partial^2 G}{\partial T \partial X} \right) X \quad (21a)$$

$$x = - \left(\frac{\partial^2 G}{\partial T \partial X} \right) \theta - \left(\frac{\partial^2 G}{\partial X^2} \right) X \quad (21b)$$

or

$$S = \frac{C_p}{T} \theta + \alpha_L X \quad (22a)$$

$$x = \alpha_L \theta + s^E X \quad (22b)$$

where the following notations are used, and denoted as C_p “heat capacitance per volume” under $X = 0$ and $E = 0$, s^E elastic compliance under constant E :

$$\begin{cases} C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{X,E} \\ s^E = - \left(\frac{\partial^2 G}{\partial X^2} \right)_{E,T} \\ \alpha_L = - \left(\frac{\partial^2 G}{\partial T \partial X} \right)_E \end{cases} \quad (23)$$

Let us discuss here the diagonal expansion coefficient $-\left(\frac{\partial^2 G}{\partial T^2} \right)$ in terms of specific heat capacity. Recall the relation $dq = T dS$ in the “reversible” thermal process, where dq is the thermal energy flow per unit “volume”. The heat capacitance C_p is defined by

$$C_p = \frac{\partial q}{\partial T} = T \left(\frac{\partial S}{\partial T} \right)_{X,E} = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{X,E} \quad (24)$$

Here we used the relation $S = - \left(\frac{\partial G}{\partial T} \right)_{X,E}$. The “piezothermal coefficient” α_L is usually called “linear thermal expansion coefficient”, because $-\left(\frac{\partial^2 G}{\partial T \partial X} \right)_E = \left(\frac{\partial x}{\partial T} \right)$. The piezothermal coefficient α_L is originated from a non-linear elastic vibration or the anharmonic phonon interaction. This piezothermal coefficient α_L contributes to the converse effect; that is, temperature change under the stress application. Considering an adiabatic condition, Eq. (22a) gives $\frac{C_p}{T} \theta = -\alpha_L X$ or $\theta = - \left(\frac{\alpha_L}{\frac{C_p}{T}} \right) X$, which means that a sudden tensile stress generates temperature decrease. The reader might have experienced in your elementary or middle school age that you felt “cool” temperature when you touched a thick rubber band on your lip immediately after expanding it (the author liked this experiment, though I could not understand the principle correctly).

The “piezothermal coupling factor” k^{PT} can be defined from Eqs. (22a) and (22b) by

$$k^{PT^2} = \frac{(\text{Coupling factor})^2}{(\text{Product of the diagonal parameters})} = \frac{\alpha_L^2}{\left(\frac{C_p}{T} \right) s^E} \quad (25)$$

Since this coupling effect is not directly related with the ferroelectric behavior, we skip the further discussion.

Adiabatic process 2 – Electrothermal effect

When the stress is constant, $X = 0$ in Eqs. (20a) and (20c), we can obtain the following equations:

$$S = \frac{C_p^E}{T} \theta - pE \quad (26a)$$

$$D = -p\theta + \varepsilon_0 \varepsilon^X E \quad (26b)$$

where the following denotations are used, C_p^E heat capacitance (per unit volume) under $X = 0$ and $E = 0$, $\varepsilon_0 \varepsilon^X$ permittivity under constant stress X :

$$\begin{cases} C_p^E = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{X,E} \\ \varepsilon_0 \varepsilon^X = - \left(\frac{\partial^2 G}{\partial E^2} \right)_{T,X} \\ p = \left(\frac{\partial^2 G}{\partial T \partial E} \right)_X \end{cases} \quad (27)$$

The primary “electrothermal coupling coefficient” p is usually called “pyroelectric coefficient”, defined by

$$p = \left(\frac{\partial^2 G}{\partial T \partial E} \right)_X = - \left(\frac{\partial P}{\partial T} \right)_X, \quad (28)$$

where we used intentionally the relation $\left(\frac{\partial G}{\partial E} \right)_X = D (\approx P)$, since the permittivity ε^X is large in ferroelectrics.

We can denote the primary “electrothermal coupling factor” k^{ET} from Eqs. (26a) and (26b) as

$$k^{ET^2} = \frac{(\text{Coupling factor})^2}{(\text{Product of the diagonal parameters})} = \frac{p^2}{\left(\frac{C_p^E}{T} \right) \varepsilon_0 \varepsilon^X} \quad (29)$$

A typical value of the electrothermal coupling factor in PZT is calculated as follows:

$$k^{ET^2} = \frac{p^2}{\left(\frac{C_p^E}{T} \right) \varepsilon_0 \varepsilon^X} = 1.11 \times 10^{-6}, \text{ or } k^{ET} = 0.105\%.$$

Using the above k^{ET^2} , we can obtain constraint heat capacitance and permittivity as follows:

- Heat capacitance under open- or short-circuit condition:

$$C_p^D = C_p^E (1 - k^{ET^2}) \quad (30)$$

- Permittivity under adiabatic or isothermal condition:

$$\varepsilon_0 \varepsilon^{X,S} = \varepsilon_0 \varepsilon^{X,T} (1 - k^{ET^2}) \quad (31)$$

Taking into account a typical value of k^{ET^2} above (i.e., unmeasurable to distinguish), the “electrothermal coupling” may not need to be considered seriously in practical experiments.

“Pyroelectric” and “electrocaloric effects”, however, exhibit promising applications at present. Electrocaloric effect was initially the focus of significant application interest in the 1940s (during World War II). The US and Japan accelerated the research for developing the air-cooling system particularly in submarines without generating mechanical noise (like air-compressor-embedded refrigerators). The recent interest comes from the energy saving by replacing the current refrigerators. Eq. (26a) gives the necessary formula for the electrocaloric effect. When we take “adiabatic” condition; that is, $dQ = TdS = 0$, or constant entropy $dS = 0$,

$$\theta = \frac{pT}{C_p^E} E \quad (32)$$

Here, C_p^E is heat capacitance per unit volume under $E = 0$, and p is “pyroelectric coefficient” given by $p = - \left(\frac{\partial P}{\partial T} \right)_X$. Decreasing temperature requires large negative electric field. In order to escape from the electric “depoling”, we usually initially increase the electric field gradually (isothermally), then make it short-circuit suddenly (adiabatically).

Isothermal process – Piezoelectric coupling**Piezoelectric constitutive equations**

When the temperature is constant (i.e., “isothermal”), $\theta = 0$ in Eqs. (20b) and (20c), we can obtain the “intensive” parameter-based “piezoelectric constitutive equations”:

$$x = s^E X + dE \quad (33a)$$

$$D = dX + \varepsilon_0 \varepsilon^X E \quad (33b)$$

where the following denotations are used, s^E elastic compliance under constant E , $\varepsilon_0 \varepsilon^X$ dielectric permittivity under stress free:

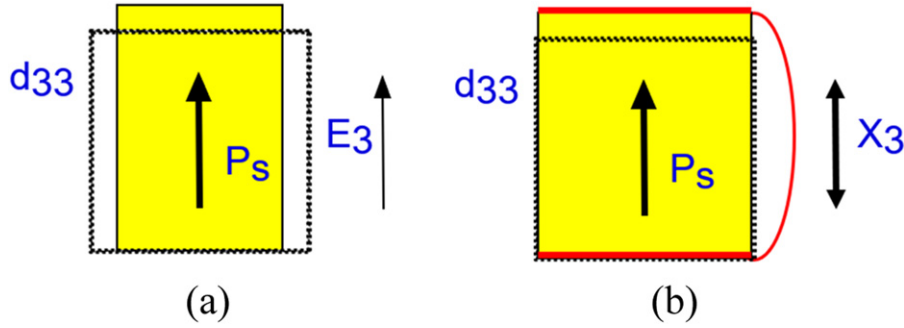


Fig. 13 Calculation models of electro-mechanical coupling factor k for (a) electric input under stress free, and (b) stress input under short-circuit condition.

$$\left\{ \begin{array}{l} s^E = - \left(\frac{\partial^2 G}{\partial X^2} \right) \\ \epsilon_0 \epsilon^X = - \left(\frac{\partial^2 G}{\partial E^2} \right) \\ d = - \left(\frac{\partial^2 G}{\partial X \partial E} \right) \end{array} \right\} \quad (34)$$

The Maxwell relation, $\left(\frac{\partial D}{\partial X} \right)_{T,E} = \left(\frac{\partial x}{\partial E} \right)_{T,X}$ verifies that the piezoelectric coefficient d in Eqs. (33a) and (33b) are thermodynamically the same.

When we start from the Helmholtz free energy A ($dA = -SdT + Xdx + EdD$), by taking a similar Taylor expansion approach, we obtain another set of piezoelectric constitutive equations in terms of “extensive” parameters, x and D :

$$X = c^D x - hD, \quad (35a)$$

$$E = -hx + \kappa_0 \kappa^X D, \quad (35b)$$

where c^D is elastic stiffness under constant D , and $\kappa_0 \kappa^X$ is inverse permittivity ($\kappa_0 = 1/\epsilon_0$) under strain free condition, and these coefficients are expressed by:

$$\left\{ \begin{array}{l} c^D = \left(\frac{\partial^2 A}{\partial x^2} \right) \\ \kappa_0 \kappa^X = \left(\frac{\partial^2 A}{\partial D^2} \right) \\ h = - \left(\frac{\partial^2 A}{\partial x \partial D} \right) \end{array} \right\} \quad (36)$$

The Maxwell relation, $\left(\frac{\partial X}{\partial D} \right)_{T,x} = \left(\frac{\partial E}{\partial x} \right)_{T,D}$, also verifies that the inverse piezoelectric coefficient h in Eqs. (35a) and (35b) are thermodynamically the same.

Electromechanical coupling factor

The term, “electromechanical coupling factor” k , is defined as the square value k^2 be the ratio of the converted energy over the input energy: when electric to mechanical

$$k^2 = (\text{Stored mechanical energy} / \text{Input electrical energy}), \quad (37a)$$

or when mechanical to electric,

$$k^2 = (\text{Stored electrical energy} / \text{Input mechanical energy}) \quad (37b)$$

Let us derive Eq. (37a) first practically, when an external electric field E_3 is applied to a piezoelectric material in a pseudo-static process. See Fig. 13(a), when we apply electric field on the top and bottom electrodes under stress free condition ($X = 0$). Input electric energy must be equal to $(1/2)\epsilon_0 \epsilon_3^X E_3^2$, and the output strain generated by E_3 should be $d_{33} E_3$. Since the converted/stored mechanical energy is obtained as $(1/2)s_{33}^E x_3^2$, we obtain:

$$k_{33}^2 = [(1/2)(d_{33} E_3)^2 / s_{33}^E] / [(1/2)\epsilon_0 \epsilon_3^X E_3^2] = d_{33}^2 / \epsilon_0 \epsilon_3^X \cdot s_{33}^E. \quad (38a)$$

Let us now consider Eq. (37b), when an external stress X_3 is applied to a piezoelectric material in a pseudo-static process. Refer to Fig. 13(b). Under short-circuit condition ($E_3 = 0$), the input mechanical energy must be equal to $(1/2)s_{33}^E X_3^2$ and the electric displacement D_3 (or polarization P_3) generated by X_3 should be equal to $d_{33} X_3$ from Eq. (33b). This D_3 can be obtained by integrating the short-circuit current in terms of time through the electric lead. Since the converted/stored electric energy is obtained as $(1/2\epsilon_0 \epsilon_3^X) D_3^2$, we obtain:

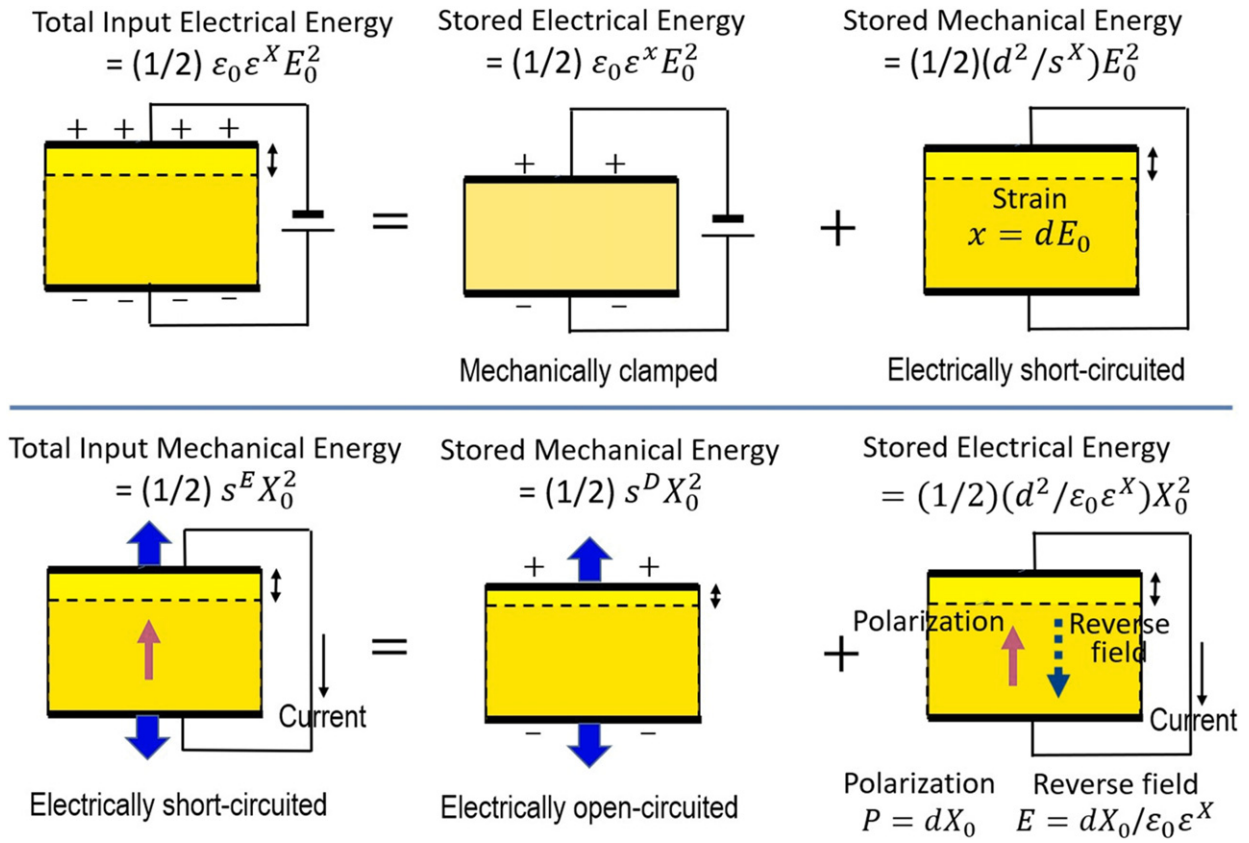


Fig. 14 Schematic representation of the response of a piezoelectric material under: (a) constant applied electric field and (b) constant applied stress conditions.

$$k_{33}^2 = [(1/2) \epsilon_0 \epsilon_3^X (d_{33} X_3)^2] / [(1/2) s_{33}^E X_3^2] = d_{33}^2 / \epsilon_0 \epsilon_3^X \cdot s_{33}^E. \quad (38b)$$

It is essential to understand that the electromechanical coupling factor k or k^2 (energy transduction or conversion rate) can be exactly the same for both converse (38a) and direct (38b) piezoelectric effects. The conditions under constant X (free stress) or constant E (short-circuit) are considered to be unconstrained.

Constraint physical parameters – Permittivity and elastic compliance

It is important to consider the constraint conditions under which a material will be operated when characterizing the dielectric constant and elastic compliance of that material (Uchino, 2009). When a constant electric field is applied to a piezoelectric sample as illustrated in Fig. 14 Top, the total input electric energy (left) should be equal to a combination of the energies associated with two distinct mechanical conditions that may be applied to the material: (1) stored electric energy under the “mechanically clamped state”, where a constant strain (zero strain) is maintained and the specimen cannot deform, and (2) converted mechanical energy under the “mechanically free state”, in which the material is not constrained and is free to deform. This situation can be expressed (1D case for simplicity) by:

$$\left(\frac{1}{2}\right) \epsilon^X \epsilon_0 E_0^2 = \left(\frac{1}{2}\right) \epsilon^x \epsilon_0 E_0^2 + \left(\frac{1}{2s^E}\right) x^2 = \left(\frac{1}{2}\right) \epsilon^x \epsilon_0 E_0^2 + \left(\frac{1}{2s^E}\right) (dE_0)^2$$

such that:

$$\epsilon^X \epsilon_0 = \epsilon^x \epsilon_0 + \left(\frac{d^2}{s^E}\right) \text{ or}$$

$$\epsilon^x = \epsilon^X (1 - k^2) \left[k^2 = \frac{d^2}{\epsilon^X \epsilon_0 s^E} \right] \quad (39a)$$

When a constant stress is applied to the piezoelectric as illustrated in Fig. 14 Bottom, the total mechanical energy will be a combination of (1) stored mechanical energy under the “open-circuit state”, and (2) converted electric energy (i.e., “depolarization field”) under the “short-circuit condition”. This can be expressed as:

$$\left(\frac{1}{2}\right) s^E X_0^2 = \left(\frac{1}{2}\right) s^D X_0^2 + \left(\frac{1}{2}\right) \epsilon^X \epsilon_0 E^2 = \left(\frac{1}{2}\right) s^D X_0^2 + \left(\frac{1}{2}\right) \epsilon^X \epsilon_0 (d / \epsilon_0 \epsilon^X)^2 X_0^2$$

which leads to:

$$s^E = s^D + \left(\frac{d^2}{\varepsilon^X \varepsilon_0} \right) \text{ or } s^D = s^E (1 - k^2) \left[k^2 = \frac{d^2}{\varepsilon^X \varepsilon_0 s^E} \right] \quad (39b)$$

In principle, if we measure the permittivity in a piezoelectric specimen under stress-free and completely-clamped conditions, we can obtain ε^X and ε^x , respectively. Similarly, if we measure the strain in a piezoelectric specimen as a function of applied stress pseudo-statically, under short-circuit and open-circuit conditions, we can obtain s^E and s^D , respectively. Note here that because typical electromechanical coupling factors are $k_{33}^2 = 50\%$ (large!) in popular PZTs, the difference of elastic compliance and permittivity between constraint and unconstraint specimens are significant; that is, doubled difference can be experimentally obtained.

We can also write equations of similar form for the corresponding reciprocal quantities:

$$\left\{ \begin{array}{l} \kappa^X / \kappa^x = (1 - k^2) \\ c^E / c^D = (1 - k^2) \end{array} \right\} \left[k^2 = \frac{h^2}{c^D (\kappa_0 \kappa^x)} \right] \quad (40)$$

The above parameter k in Eq. (40) is also the “electromechanical coupling factor” in the “extensive” parameter description, and identical to the k in . Note the k expression derivation from the piezoelectric constitutive equations, Eqs. (33a), (33b), (35a) and (35b):

$$k^2 = \frac{(\text{Coupling factor})^2}{(\text{Product of the diagonal parameters})} = \frac{d^2}{s^E \varepsilon^X \varepsilon_0} = \frac{h^2}{c^D (\kappa_0 \kappa^x)} \quad [\kappa_0 = 1/\varepsilon_0] \quad (41)$$

Non-Linear Coupling in Ferroelectrics

“Order parameter”, polarization P , distinguishes paraelectric ($P = 0$) and ferroelectric phases ($P \neq 0$) by considering the nonlinear coupling in phenomenology.

Landau phenomenology

Starting from one order parameter P , we consider the Taylor expansion of the Landau free energy:

$$\begin{aligned} F(P) &= F(0) + \left(\frac{\partial F}{\partial P} \right) P + \frac{1}{2} \left(\frac{\partial^2 F}{\partial P^2} \right) P^2 + \frac{1}{6} \left(\frac{\partial^3 F}{\partial P^3} \right) P^3 + \frac{1}{24} \left(\frac{\partial^4 F}{\partial P^4} \right) P^4 + \frac{1}{120} \left(\frac{\partial^5 F}{\partial P^5} \right) P^5 + \dots \\ &= F(0) + a_1 P + a_2 P^2 + a_3 P^3 + a_4 P^4 + a_5 P^5 + a_6 P^6 \dots \end{aligned} \quad (42)$$

We assume that energy description is common through the paraelectric and ferroelectric phases, thus that the reduction of the Taylor expansion terms follows to the highest symmetry paraelectric phase. When the paraelectric phase is “centro-symmetric” (like a perovskite ferroelectric), odd-power of the expansion tensor coefficient a_i becomes “zero”. In other words, the free energy formula of the crystal should maintain with polarization reversal ($P \rightarrow -P$) in order to keep the charge or capacitance constant, regardless of the specimen orientation/up-side-down. The condition $F(P) = F(-P)$ also makes the odd-power terms of P disappear. Thus, the expansion series include only even powers of P :

$$F(P) = a_2 P^2 + a_4 P^4 + a_6 P^6 \dots \quad (43)$$

We usually handle the Landau free energy F till the P^6 term in “Landau Theory” in 1D represented formula (i.e., “first-order transition”). However, we describe here only two terms of P^4 in the simplest formula (i.e., “second-order transition”) below:

$$F(P, T) = \left(\frac{1}{2} \right) \alpha P^2 + \left(\frac{1}{4} \right) \beta P^4 \quad (44)$$

The coefficients α and β depend, in general, on the temperature. However, taking only the first coupling term ($T \cdot P^2$) into account, only α is assumed to be temperature dependent in the following formula:

$$\alpha = (T - T_0) / \varepsilon_0 C, \quad (45)$$

where the proportional constant C is called the “Curie-Weiss constant” and T_0 (“Curie-Weiss temperature”) is equal to or lower than the actual transition temperature T_C (“Curie temperature”) in general. The parameter β should be positive in order to stabilize finite polarization in the second-order transition formula. Recall Eq. (10), which was introduced originated from the polarizability linear change with temperature; that is equivalent to Eq. (45). Because of the assumption that the phenomenological formulation should be applied for the whole temperature range over which the material is in the paraelectric and ferroelectric states, and that the spontaneous polarization should be zero in the paraelectric state, the free energy should be zero in the paraelectric phase at any temperatures above its phase transition temperature (i.e., “Curie temperature”). To stabilize the ferroelectric state with a spontaneous polarization, the free energy for a finite polarization P should be lower than “zero”. Otherwise, the paraelectric state should be maintained. Thus, at least, the coefficient α of the P^2 term must be negative for the polarized state to be stable; while in the paraelectric state it must be positive passing through zero at some temperature T_0 (“Curie-Weiss temperature”). Introduction of Eq. (45) supports the above concept.

From the free energy definition $dF = -SdT + EdP$, the equilibrium polarization under an electric field E should satisfy the following condition:

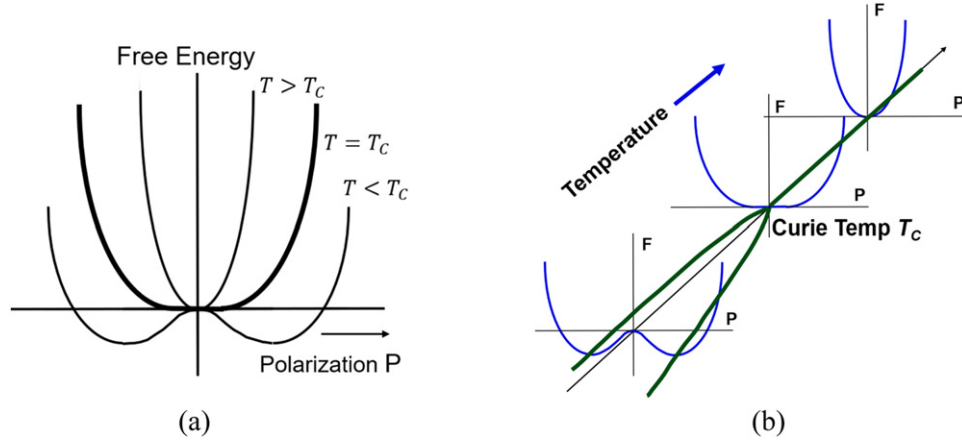


Fig. 15 Landau free energy change associated with the second-order phase transitions: (a) projected curves on F - P domain and (b) extended description with temperature axis.

$$\left(\frac{\partial F}{\partial P}\right) = E = \alpha P + \beta P^3 \quad (46)$$

With no electric field applied, Eq. (46) [$P(\alpha + \beta P^2) = 0$] provides two cases:

$$(i) P = 0, \text{ and } (ii) \alpha + \beta P^2 = 0$$

The case (i) provides the trivial solution corresponding to a paraelectric state; while the case (ii) reveals a finite polarization solution corresponds to a ferroelectric state, $P^2 = -\alpha/\beta$. Since β is positive, $\alpha < 0$ or $T < T_0$ is required to stabilize the solution, which is satisfied in the ferroelectric phase. Two roots, $P = \pm \sqrt{-\alpha/\beta}$, correspond to upward and downward two spontaneous polarization states.

Devonshire phenomenology

As mentioned in Section "Landau Phenomenology", in a ferroelectric whose prototype phase (high temperature paraelectric phase) is centrosymmetric and non-piezoelectric, the piezoelectric coupling term ($P \cdot X$) is omitted and only the "electrostrictive coupling" term ($P^2 \cdot X$) is introduced (in order to satisfy the energy equivalency with polarization reversal $P \rightarrow -P$). Note that stress X is a tensor, coordinate inversion does not change the sign. The theories for electrostriction in ferroelectrics were formulated in the 1950s by Devonshire (1949, 1954) and Kay (1955). Let us assume that the "elastic Gibbs energy" ($dG_1 = -SdT - x dX + E dP$) should be expanded in a 1D form:

$$G_1(P, X, T) = \left(\frac{1}{2}\right)\alpha P^2 + \left(\frac{1}{4}\right)\beta P^4 - \left(\frac{1}{2}\right)sX^2 - QP^2 \cdot X, [\alpha = (T - T_0)/\epsilon_0 C] \quad (47)$$

Where P , X , T are the polarization, stress and temperature, respectively, and s and Q are called the elastic compliance and electrostrictive coefficient, respectively. This leads to the following Eqs. (48)–(50):

$$E = \left(\frac{\partial G_1}{\partial P}\right) = \alpha P + \beta P^3 - 2QPX \quad (48a)$$

$$x = -\left(\frac{\partial G_1}{\partial X}\right) = sX + QP^2 \quad (48b)$$

$$(1/\epsilon_0 \epsilon) = \left(\frac{\partial E}{\partial P}\right) = \alpha + 3\beta P^2 - 2QX \quad (48c)$$

(a) When the external stress is zero, the following equations are derived:

$$E = \alpha P + \beta P^3 \quad (49a)$$

$$x = QP^2 \quad (49b)$$

$$(1/\epsilon_0 \epsilon) = \alpha + 3\beta P^2 \quad (49c)$$

If the external electric field E is equal to zero, two different states are derived; $P = 0$, and $\alpha + \beta P^2 = 0$. Fig. 15(a) illustrates free energy curves plotted for the second-order phase transition at higher and lower temperatures than the phase transition point, "Curie temperature". When $\alpha < 0$ (i.e., $T < T_c = T_0$ in this case), the double minima of the free energy appear, which correspond to $\pm P_s$. Landau free energy change is shown in an extended form in terms of temperature in Fig. 15(b), where the reader can notice the energy minimum point tracing line, which splits into two lines from single line, like a "Y-shape fork", at the phase transition

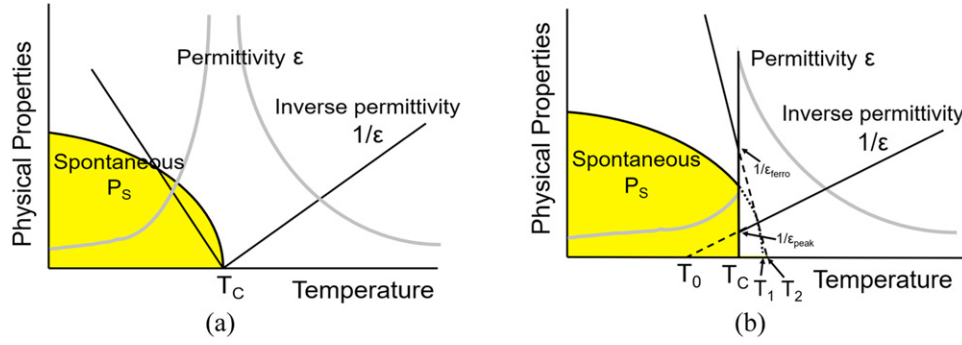


Fig. 16 Spontaneous polarization and permittivity change associated with the second-order (a) and the first-order (b) phase transitions in a ferroelectric.

temperature $T_C = T_0$, which is called “bifurcation”. The “bifurcation parameter”, in this case “ α ” of a system, causes a sudden topological change in its behavioral contour. The occurrence of the double minima generates the hysteresis curve in the P - E loop.

(i) Paraelectric phase: $P_S = 0$ or $P = \epsilon_0 \epsilon E$ (under small E).

Permittivity:

$$\epsilon = C/(T - T_0) \quad (\text{Curie - Weiss law}) \quad (50)$$

Electrostriction:

$$x = Q(\epsilon_0 \epsilon)^2 E^2 \quad (51)$$

The conventional electrostrictive coefficient M , defined by $x = ME^2$, is related to the electrostrictive Q coefficient through $M = Q(\epsilon_0 \epsilon)^2$.

(ii) Ferroelectric phase: $P_S^2 = -\alpha/\beta$ or $P = P_S + \epsilon_0 \epsilon E$ (under small E)

$$x = Q(P_S + \epsilon_0 \epsilon E)^2 = QP_S^2 + 2QP_S \epsilon_0 \epsilon E + Q(\epsilon_0 \epsilon)^2 E^2$$

where we define the spontaneous strain x_S and the piezoelectric constant d as:

Spontaneous strain:

$$x_S = QP_S^2 \quad (52)$$

Piezoelectric constant:

$$d = 2QP_S \epsilon_0 \epsilon \quad (53)$$

The reader can understand that the spontaneous polarization creates a “piezoelectric effect” in a ferroelectric phase through the electromechanical (i.e., “electrostrictive effect”) coupling. Fig. 16(a) illustrates the spontaneous polarization and permittivity change with temperature in the second-order phase transition of a ferroelectric.

(b) When the external stress X is applied on a ferroelectric without the external electric field E (note $\alpha P_S + \beta P_S^3 = 0$), Eq. (48a) indicates the “reverse electric field” (i.e., “depolarization field”) generation:

$$E = -2QP_S X \quad (54)$$

Taking Eq. (54) into the constitutive equation Eq. (33b), $D = dX + \epsilon_0 \epsilon^X E$ under $D = 0$ condition (i.e., “open-circuit”), we obtain

$$dX = -\epsilon_0 \epsilon^X E = -\epsilon_0 \epsilon^X (-2QP_S X) = P, \quad (55)$$

leading to the relation Eq. (53):

$$d = 2QP_S \epsilon_0 \epsilon$$

Eq. (55) corresponds to the “direct piezoelectric effect”.

To the contrary, in a paraelectric phase ($P_S = 0$), the reader can derive that no polarization is induced under the external stress, but the permittivity (first derivative of polarization in terms of electric field) is modulated (Eq. 48c); the “inverse permittivity changes linearly with stress” because of the electrostrictive coupling $P^2 X$:

$$(1/\epsilon_0 \epsilon) = \alpha - 2QX = (T - T_0 - 2Q\epsilon_0 CX)/\epsilon_0 C \quad (56)$$

This is the “converse electrostrictive effect” in the paraelectric phase. Because hydraulic compressive pressure (i.e., negative stress) decreases the Curie temperature by 50°C/GPa in most of perovskite ferroelectrics, (Samara, 1970) the permittivity is decreased according to the phase transition temperature decrease.

Though we basically skip the description on the first-order phase transition of the phenomenology with integrating $(\frac{1}{6})\gamma P^6$ term in this article, the spontaneous polarization and permittivity change associated with the phase transitions is illustrated in Fig. 16(b) for the reader’s sake, where differences from (a) include: (1) The Curie temperature T_C is higher than the Curie-Weiss temperature T_0 . (2) Finite permittivity at T_C . (3) Jump in the spontaneous polarization and permittivity at T_C .

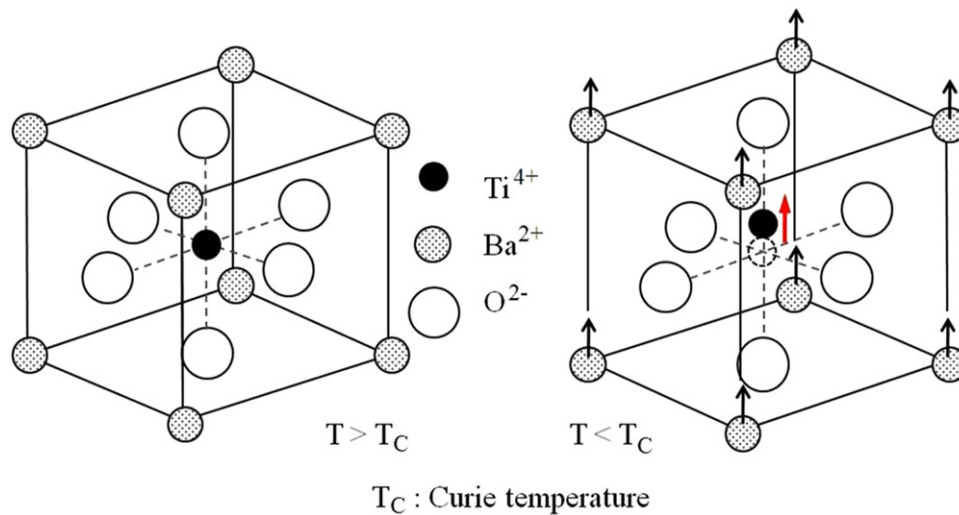


Fig. 17 Crystal structures of BaTiO₃: Higher (left) and lower (right) than T_C .

Ferroelectric Materials

History of Piezoelectrics

Quartz (SiO₂) and zinc oxide (ZnO) are popular piezoelectric, but non-ferroelectric (non-polar) materials. The “direct piezoelectric effect” was discovered in quartz by Piere and Jacques Curie in 1880. The “converse piezoelectric effect” was discovered successively in 1881 by Gabriel Lippmann. Shipwreck of Titanic and World War I were the motivation of the undersea transducer, sonar. Paul Langevin developed so-called Langenvin-type transducer, which was originally composed of natural tiny quartz single crystals sandwiched by two metal blocks, in order to tune the transducer resonance frequency around 26 kHz which is a desired range for underwater applications (Uchino, 2017).

On the other hand, the first ferroelectric discovered is Rochelle salt (NaKC₄H₄O₆•4H₂O) in 1921. Though this material was studied from an academic viewpoint, it has not been widely utilized in practice because it is water-soluble and its Curie temperature is just above room temperature. KH₂PO₄ (KDP) is the second discovery in 1935, which is also water-soluble and the Curie temperature is -150°C . We needed to wait until World War II for the third and the most famous ceramic ferroelectric, i.e., barium titanate (BaTiO₃, BT), which was actually commercialized first as a transducer material. After WW II, PbTiO₃, PbZrO₃ and their solid solution system PZT ceramics, isomorphic perovskite-type to BT, have been developed, which became the most popular industrial materials even at present. We describe on BT, PZT, relaxor ferroelectrics, polymer PVDF, and Pb-free piezoceramics in the followings.

Barium Titanate (BT)

Using BaTiO₃ (BT) as an example, we introduce basic properties of ferroelectrics. Fig. 17 shows BT crystal structure with a perovskite-type; center and corners are shared by cations Ti⁴⁺ and Ba²⁺ and the face-centers are occupied by anion O²⁻. In the high temperature paraelectric phase (non - polar phase) there is no spontaneous polarization (the symmetry is $O_h - m3m$). Below the transition temperature T_C called the Curie temperature (about 130°C), spontaneous polarization occurs, and the crystal structure becomes slightly elongated, that is, tetragonal ($C_{4v} - 4mm$). Recall the dipole coupling energy discussed in Section “Local Electric Field and Dipole Coupling Energy” for the spontaneous ionic shifts. The temperature dependence of the spontaneous polarization P_s and permittivity (dielectric constant) ϵ in BT is schematically the same as the “first phase transition” shown in Fig. 16(b). With decreasing temperature from room temperature, however, BT undergoes a series of complicated phase transitions. Fig. 18 illustrates these successive phase transitions in terms of dielectric constant from Cubic, Tetragonal, Orthorhombic, and Rhombohedral phases with a decrease in temperature (Uchino, 2009).

We describe here the material’s designing strategy on the Curie temperature T_C from the application viewpoints; T_C for capacitor materials is designed to set around room temperature (RT) so that the maximum permittivity is obtained around RT; T_C for memory materials around 100°C higher than RT; T_C for pyroelectric sensors just above RT so that a large slope $p = -\frac{\partial P_s}{\partial T}$ is expected; T_C for piezoelectric transducers typically much higher than RT, higher than 200°C to stabilize the poled state under high vibration condition; T_C for electrooptic (Kerr effect) and electrostrictive devices are slightly lower than RT to use their paraelectric state. Note that BT-based ceramics are the current majority ceramic capacitor materials, though the piezoelectric transducers are made of PZTs.

Lead Zirconate Titanate (PZT)

Lead zirconate titanate (PZT) solid solution systems among PbTiO₃ and PbZrO₃ were discovered in 1954 by Japanese researchers, Shirane, Sawaguchi and Takagi (Sawaguchi *et al.*, 1951). Fig. 19(a) shows the phase diagram of lead zirconate titanate (PZT), where the

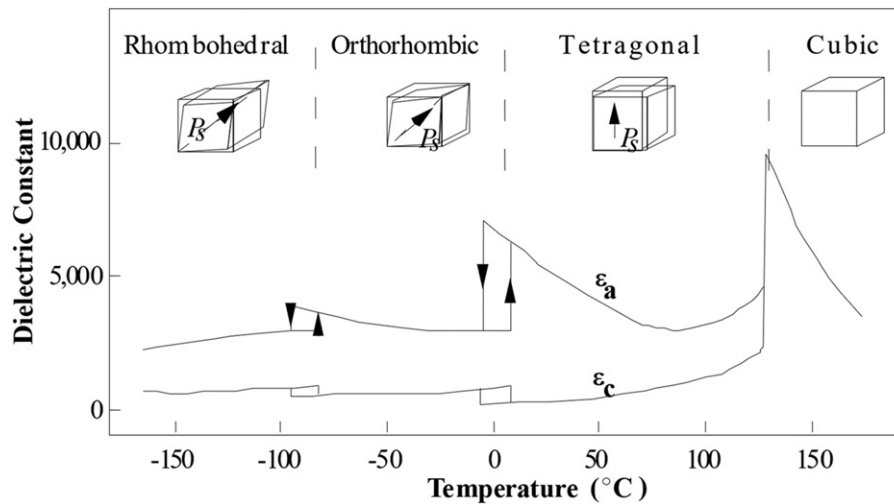


Fig. 18 Various phase transitions in barium titanate (BT). Reproduced from Uchino, K., 2009. *Ferroelectric Devices*, second ed. New York: CRC Press.

“Morphotropic Phase Boundary (MPB)” between the tetragonal and rhombohedral phases exists around 52 PZ - 48 PT compositions. However, the enormous piezoelectric properties were discovered by Jaffe (1955), Clevite Corporation, thus Clevite took the most important PZT patent for transducer applications. Because of this strong basic patent, Japanese ceramic companies were actually encouraged to develop ternary systems to overcome the performance, and more importantly, to escape from the Clevite’s patent; that is, PZT + a complex perovskite such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (Matsushita Panasonic), $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (NEC), $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (Toshiba), which are the basic compositions in recent years. Fig. 19(b) plots the dependence of several piezoelectric d constants on composition near the morphotropic phase boundary in the PZT system. Note that the maximum piezoelectric performance is obtained around the MPB composition in the pure PZT solid solution system. This is why the PZTs share the majority of the industrial applications at present.

Relaxor Ferroelectrics

Relaxor ferroelectrics can be prepared either in polycrystalline form or as single crystals. Different from the previously mentioned normal ferroelectrics, the relaxor-types exhibit a “broad phase transition” from the paraelectric to ferroelectric state, a “strong frequency dependence of the dielectric constant” (i.e., “dielectric relaxation”) and a weak remanent polarization. Most of lead-based relaxor materials have complex disordered perovskite structures.

Relaxor-type electrostrictive materials, such as those from the lead magnesium niobate - lead titanate, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (or PMN-PT), solid solution are highly suitable for both (1) capacitor, and (b) actuator applications. The permittivity of the relaxor ferroelectrics reaches 10,000, that is, 10 times higher than the BT based capacitor materials. Fig. 20(a) and (b) show typical strain curves for a piezoelectric lead zirconate titanate (PZT) based and an electrostrictive lead magnesium niobate (PMN) based ceramic (Uchino *et al.*, 1981; Uchino, 1986). An almost linear strain curve in PZT becomes distorted and shows large hysteresis with increasing applied electric field level, which is due to the polarization reorientation (Fig. 20(a)). On the other hand, PMN does not exhibit hysteresis under an electric field cycle. However, the strain curve deviates from the quadratic relation (E^2) at a high electric field level (Fig. 20(b)). Note a gigantic electrostriction higher than 0.1%, even in the secondary electromechanical coupling by the author’s group, which triggered the research fever on “ceramic actuators” in the early 1980s.

This electrostrictive relaxor also exhibits an induced piezoelectric effect. That is, the electromechanical coupling factor k_t varies with the applied DC bias field. The effective piezoelectric coefficient is obtained by the strain slope with electric field ($\frac{\partial \lambda}{\partial E}$) in Fig. 20(b). As the DC bias field increases, the strain slope increases significantly and saturates. Since this behavior is reproducible (no observable hysteresis), these materials can be applied as ultrasonic transducers which are tunable by the bias electric field (Takeuchi *et al.*, 1990).

In parallel, the author’s group discovered single-crystal relaxor ferroelectrics with the morphotropic phase boundary (MPB) composition in the late 1970s, which show tremendous promise as ultrasonic transducers and electro-mechanical actuators (Kuwata *et al.*, 1982). Single crystals of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), and binary systems of these materials combined with PbTiO_3 (PZN-PT and PMN-PT) exhibit extremely large electromechanical coupling factors (Kuwata *et al.*, 1982; Shrout *et al.*, 1990). Large coupling coefficients and large piezoelectric constants have been discovered for crystals from the morphotropic phase boundaries of these solid solutions. PZN-8%PT single crystals were found to possess a high k_{33} value of 0.94 for the $\langle 001 \rangle$ crystal cuts; this is very high compared to the k_{33} of conventional PZT ceramics of around 0.70–0.80. We pointed out that the extraordinary large k_{33}^{eff} is obtained in the rhombohedral phase when the electric field is canted 57° from the rhombohedral spontaneous polarization direction, that has motivated the research direction to so-called “domain engineering”.

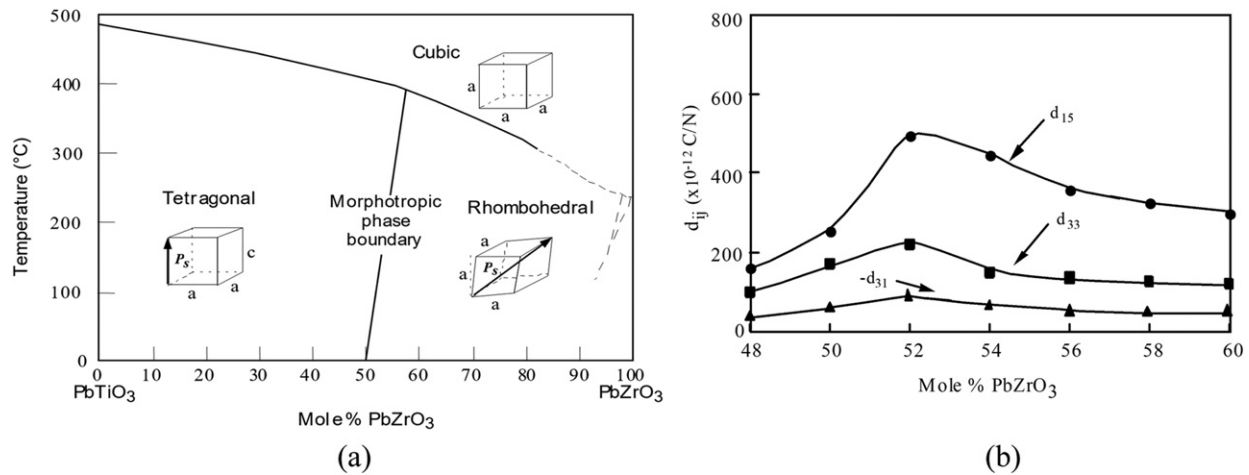


Fig. 19 (a) Phase diagram of lead zirconate titanate (PZT). (b) The d constant change with composition near the MPB in the PZT system. Reproduced from (a) Sawaguchi, E., Shirane, G., Takagi, Y., 1951. Phase transition in lead zirconate. *J. Phys. Soc. Jpn.* 6, 333–339. (b) Jaffe, B., 1955. Piezoelectric transducers using lead titanate and lead zirconate, US Patent 2,708,244, May (1955).

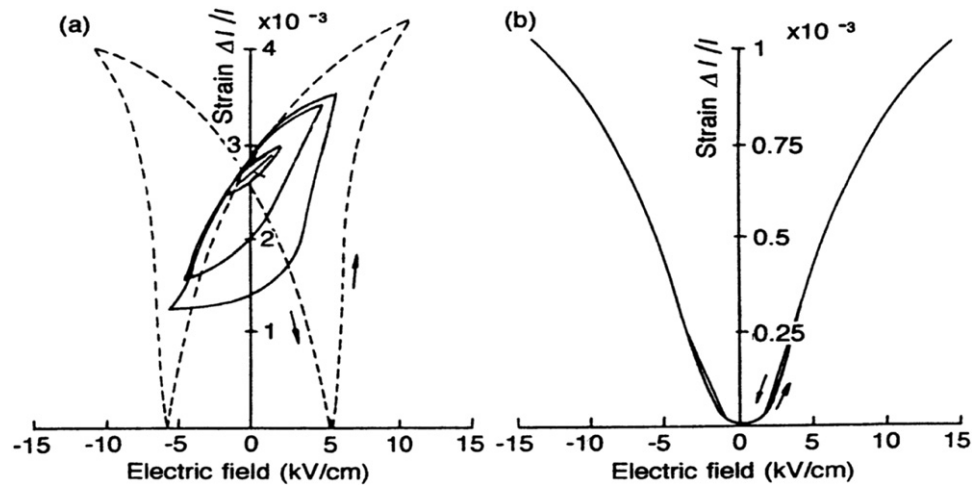


Fig. 20 Typical strain curves for a piezoelectric lead zirconate titanate (PZT) based (a) and an electrostrictive lead magnesium niobate (PMN) based ceramic (b). Reproduced from (b) Uchino, K., 1986. *Electrostrictive Actuators: Materials and Applications*. *Bull. Am. Ceram. Soc.* 65 (4), 647.

PVDF

Thank to Kawai's efforts, "polyvinylidene difluoride" (PVDF or PVF₂) was discovered in 1969 (Kawai, 1969). Though the piezoelectric d constant is not as high as piezo-ceramics, high piezoelectric g constant due to small permittivity is attractive from the sensor application viewpoint. The PVDF is a polymer with monomers of CH₂CF₂. Since H and F atoms have positive and negative ionization tendency (though covalent bonding basically), the monomer itself has a dipole moment. Crystallization from the melt forms the non-polar α -phase, which can be converted into the polar β -phase by a uniaxial or biaxial drawing operation; the resulting dipoles are then reoriented through electric poling (see Fig. 21, which give the upward dipole direction).

Another intriguing advantage is polymer's manufacturability: large sheets can be prepared and thermally formed into complex shapes. Piezoelectric polymers have the following characteristics: (a) small piezoelectric d constants (for actuators) and large g constants (for sensors), (b) light weight and soft elasticity, leading to good "acoustic impedance matching" Z with water or the human body, (c) a low mechanical quality factor Q_{mv} allowing for a broad resonance band width, though the heat generation is problematic during continuous operation.

Pb-Free Piezo-Ceramics

European community started RoHS (Restrictions on the use of certain Hazardous Substances) from 2006, that explicitly limits the usage of lead (Pb) in electronic equipment. Basically, we may need to regulate the usage of lead zirconate titanate (PZT), current

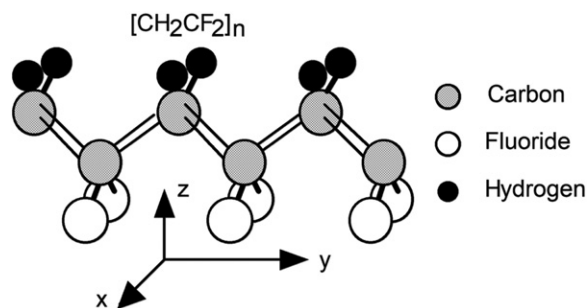


Fig. 21 Molecular structure of polyvinylidene difluoride (PVDF).

most famous piezoelectric ceramics, in the future. Japanese and European community may experience governmental regulation on the PZT usage in these 10 years. Pb (lead)-free piezoceramics have started to be developed after 1999. The Pb-free materials include (1) $(\text{K,Na})(\text{Ta,Nb})\text{O}_3$ based, (2) $(\text{Bi,Na})\text{TiO}_3$, and (3) BaTiO_3 , which reminds us “the history will repeat” (i.e., ‘piezoelectric Renaissance’). Though their piezoelectric performances are inferior to the PZTs in general, the government regulation may affect stronger than the conventional performance-oriented research motivation.

Applications of Ferroelectrics

General Application Trends

Ferroelectric materials, especially polycrystalline ceramics, are very promising for a variety of applications such as high permittivity capacitors, ferroelectric memories, pyroelectric sensors, piezoelectric and electrostrictive transducers, electrooptic devices and PTC thermistors. Refer to [Uchino \(2009\)](#) for the detailed discussions.

For capacitor dielectrics, the peak dielectric constant around the transition (i.e., Curie) temperature is utilized, while for memory applications, the material must be ferroelectric at room temperature. A large temperature dependence of the spontaneous polarization just below T_C is sought for pyroelectric sensors. The converse pyroelectric effect is the electrocaloric effect (sudden negative electric field generates the temperature decrease), which is becoming a hot research topic in this energy saving sustainable age.

Piezoelectric materials are used as both sensors and actuators, where the T_C should be much above room temperature. Pressure and acceleration sensors are now commercially available in addition to conventional piezo-vibrators (speakers, sounders). Precision positioners and pulse drive linear motors have already been installed in precision lathe machines, semiconductor manufacturing apparatuses and office equipment. Recent enthusiastic development is found in ultrasonic motors, aiming at “electromagnetic and sound noise”-free, and very compact motor applications. Recently, in parallel to the new energy source programs, piezoelectric energy harvesting systems became popular. Waste mechanical energy such as noise vibration, wind, human walk can be converted into electrical energy to directly use for signal transmission or to charge up batteries for portable electronics. Our development strategy is to “eliminate traditional batteries”, which are classified as hazardous wastes, but recycled by less than 0.5% of 10s Billion batteries sold per year in the world.

Electrooptic materials will become key components in displays and optical communication systems in the near future. Optical beam scanners, light valves and switches are urgent necessities for commercialization. For thermistor applications, semiconductive ferroelectric ceramics with a positive temperature coefficient of resistivity (PTCR) based on a junction effect have been developed from barium titanate based materials. These thermistors are applied world-widely for automobile engine ignitions and ceramic heaters etc.

Ferroelectric devices, however, often fail to be commercialized in the cases where competitive materials exist. In the photo-sensors, for example, semiconductive materials are superior to ferroelectrics in response speed and sensitivity. Magnetic devices and flash memories are much more popular in the memory field, and liquid crystals and LED are typically used for optical displays. From the actual worldwide revenue viewpoint, “capacitors” share more than 50%, followed by “piezoelectric devices” ~ 30%, then “PTCR thermistors” ~ 15%. Because the “piezoelectricity” is rather unique performance without finding strong competitors (electromagnetic counterpart motors/transformers are very inferior in terms of efficiency in compact component domains smaller than 30 W), piezoelectric applications are expanding significantly in these days. Though the electrooptic and pyroelectric/electrocaloric effects seem to be very intriguing personally, their revenue contributions are still very small from the industrial viewpoints at present.

Remarkable application examples are introduced in the following.

Ferroelectric Memories

There are volatile and non-volatile memory devices in erasable semiconductor memories. DRAM (Dynamic Random Access Memory), which is widely used because of its high integration capability, is a volatile memory. Data stored in the memory are lost when the electric power is shut off. On the contrary, non-volatile memories include a circuit-latch multiple FETs (“Field Effect

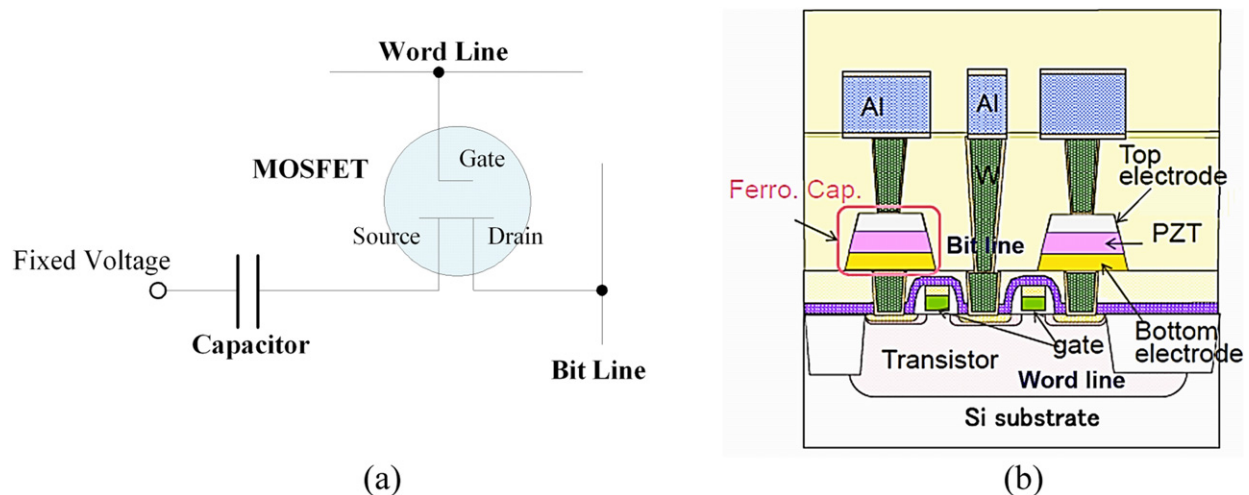


Fig. 22 (a) Fundamental structure of DRAM or FRAM, composed of a MOSFET and a capacitor. (b) FRAM fabrication process compatible to CMOS logic process. Reproduced from (b) Eshita, T., Wang, W., Sugiyama, Y., *et al.*, 2013. Development of PZT based ferroelectric capacitor for mass-production ferroelectric RAM (FRAM). In: Proceedings of the Electronic Materials and Applications (EMA), January (2013).

Transistor”) and a Si-surface-potential control MOS (Metal-Oxide-Semiconductor) FET channel. However, both types, in general, have problems in integration density and writing time (Uchino, 2009).

Fig. 22(a) shows the fundamental structure of DRAM or FRAM composed of a transistor (MOSFET) and a capacitor. If the capacitor is made of a paraelectric dielectric (traditionally SiO_2) or a ferroelectric material, volatile or non-volatile memory ($-$ or $+P_s$ state corresponds to “0” or “1”) is realized. Fig. 22(b) shows a commercialized structure of the FRAM by Fujitsu, Japan, (Eshita *et al.*, 2013) which we can find in the memory chip of American Express Credit Card, Disneyland entrance card etc. When writing, one DRAM/ FRAM element is chosen by x-y addressing; that is, voltage is applied on both the “gate” and the “drain” electrodes simultaneously, thus accumulating charge on the dielectric film capacitor (memorizing). Since the accumulated charge leaks, the capacitor must be recharged repeatedly (refreshing) in DRAM; while $-$ or $+P_s$ state can be kept for a long period in the ferroelectric, non-volatile FRAM is realized.

The electron-hole pair generation around the FET by the IC package or natural radiation changes the amount of charge on the capacitor, and sometimes destroys the memory (“soft error”). In order to retain memory, the capacitance of the memory capacitor must be higher than 30 fF (remember $f = 10^{-15}$ and called “femto”). With using a high permittivity paraelectric material, or high remnant polarization ferroelectric, we can miniaturize the DRAM/FRAM area by keeping 30 fF capacitance.

Infrared Image Sensors

Fig. 23(a) illustrates a structure of a pyro-vidicon tube, which visualizes a thermal-distribution (i.e., infrared) image (Taylor and Boot, 1973). Light emitted from an object, which should be warmer than the surrounding temperature, is filtered with a “germanium lens” producing an infrared beam (long wavelength), which is focused onto the pyroelectric target through an optical chopper. The temperature distribution of the object is represented on the target as a shrunk image, leading to a pyroelectric voltage distribution. This is monitored from the back surface of the target by electron-beam scanning using a traditional TV tube then.

One of the disadvantages of the pyro-vidicon is the degradation of the image over a long period of usage due to “thermal diffusion” on the target. From this sense, the figure of merit $p/(c_p \alpha \epsilon)$ is essential, including the thermal diffusivity α , in addition to the pyroelectric constant p and specific heat capacity c_p . The thermal diffusivity can also be improved by modifying the structure. Pedder *et al.* proposed a segmented target design to solve the diffusion problem (Warner *et al.*, 1981). Fig. 23(b) shows the microscopic structure of a D-TGS [deuterated triglycine sulfate, $(\text{ND}_2\text{CD}_2\text{COOD})_3\text{D}_2\text{SO}_4$] target, in which TGS crystal target was divided fine segments then (19 μm width, 16 μm depth, 25 μm pitch). Most recent thermal IR cameras can demonstrate temperature distribution (thermograph) around the nodal line area on piezoelectric devices, where the maximum stress and strain generate the heat via the elastic loss (Uchino, 2020).

Piezoelectric Multilayer Actuators for Automobile

Diesel engines are recommended rather than regular gasoline cars from the energy conservation and global warming viewpoint. When we consider the total energy of gasoline production, both well-to-tank and tank-to-wheel, the energy efficiency, measured by the total energy required to realize unit drive distance for a vehicle (MJ/km), is of course better for high octane gasoline than diesel oil. However, since the electric energy required for purification is significant, the gasoline is inferior to diesel fuel see “Relevant Websites section”. As well known, the conventional diesel engine, however, generates toxic exhaust gases such as SO_x and NO_x due

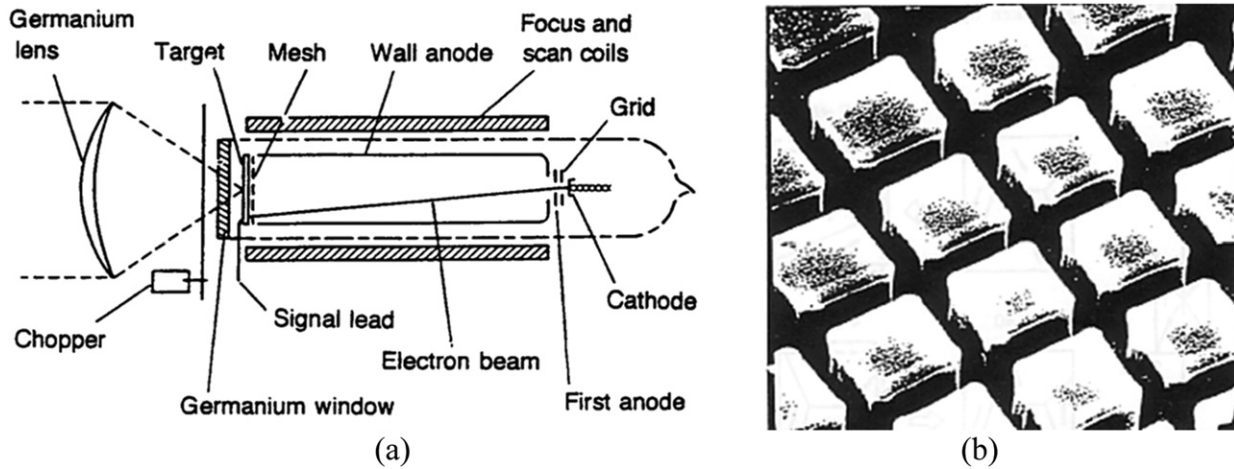


Fig. 23 (a) Structure of a pyro-vidicon tube. (b) Infrared image target of a D-TGS crystal with divided fine segments ($19\text{ }\mu\text{m}$ width, $16\text{ }\mu\text{m}$ depth, $25\text{ }\mu\text{m}$ pitch). Reproduced from (a) Taylor, R.G.F., Boot, H.A.H., 1973. *Contemp. Phys.* 14, 55. (b) Warner, D.J., Pedder, D.J., Moody, I.S., Burrage, J., 1981. *Ferroelectrics* 33, 249.

to insufficient burning of the fuel. In order to solve this problem, new diesel injection valves were developed by Siemens, Bosch and Toyota with piezoelectric multilayered (ML) actuators. Fig. 24 shows such a common-rail type diesel injection valve with a ML piezo-actuator which produces high pressure fuel and quick injection control. Owing to the large force and quick response of the PZT ML actuator, we could realize very fine mist of diesel fuel in order to be burned effectively. The highest reliability of these devices at an elevated temperature (150°C) for a long period (10 years) has been achieved (Fujii, 2005). The piezoelectric actuator is namely the key to increase burning efficiency and minimize the toxic exhaust gases. Current research target includes the Cu internal electrode usage for replacing the Ag-Pd electrode to reduce the manufacturing cost of the piezo-ML's.

Ultrasonic Motors (USM) for Camera Modules

A micro motor called "metal tube type" consisting of a metal hollow cylinder and two PZT rectangular plates was developed by The Penn State University in the late 1990s (see Fig. 25(a)). When one of the PZT plates is driven (single phase drive), Plate X, a bending vibration is excited basically along x-axis. However, because of an asymmetrical mass (Plate Y), another hybridized bending mode is excited with some phase lag along y axis, leading to an elliptical locus in a clockwise direction, like a 'Hula-Hoop' motion. The rotor of this motor is a cylindrical rod with a pair of stainless ferrules pressing down with a spring. The metal cylinder motor 2.4 mm in diameter and 12 mm in length was driven at 62.1 kHz in both rotation directions. No-load speed of 1800 rpm and output torque of up to 1.8 mN•m were obtained for rotation in both directions under an applied rms voltage of 80 V. A rather high maximum efficiency of about 28% for this small motor is a noteworthy feature (Koc et al., 2002; Cagatay et al., 2003). Various modifications were made for the stator, including a type with four PZT plates, arranged symmetrically and driven by two-phase (sine and cosine) voltages.

In collaboration with The Penn State University, Samsung Electromechanics, Korea developed a zoom and focus mechanism with two micro rotary motors in 2003. Two micro metal tube motors with 2.4 mm diameter and 14 mm length were installed to control zooming and focusing lenses independently in conjunction with screw mechanisms, as illustrated in Fig. 25(b) (Uchino, 2004). A screw is rotated through a pulley, which is then transferred to the lens up-down motion. The square chip ($3 \times 3\text{ mm}^2$) on the camera module in Fig. 25(c) is a high-frequency drive voltage supply. New Scale Technologies (Victor, NY) integrated a screw in the metal tube motor, and commercialized "squiggle motors" worldwide for camera module applications, with a partnership with ALPS, Tamron, and TDK-EPC see "Relevant Websites section". Samsung Electromechanics is now utilizing much smaller micro ML chip linear USM's for the Galaxy series camera modules due to the thinner design necessity (Koc et al., 2006).

Piezoelectric Energy Harvesting Systems

One of the recent research interests is "piezoelectric energy harvesting". Cyclic electric field excited in the piezoelectric plate by the environmental noise vibration is accumulated into a rechargeable battery. Originally we consumed the converted electrical energy via Joule heat in order to damp the vibration rapidly in the 1980s (Uchino and Ishii, 1988). After getting into the 1990s, we started to accumulate it in a rechargeable battery, which seems to be the pioneering study (Kim et al., 2004, 2005; Uchino, 2011). There are three major phases/steps associated with the piezoelectric energy harvesting development: (1) mechanical-mechanical energy transfer, including mechanical stability of the piezoelectric transducer under large stresses, and mechanical impedance matching, (2) mechanical-electrical energy transduction, relating with the electromechanical coupling factor in the composite transducer structure, and (3) electrical-electrical energy transfer, including electrical impedance matching. A suitable DC/DC converter is required to accumulate the electrical energy from a high impedance piezo-device into a rechargeable battery (low impedance) (Uchino, 2011).

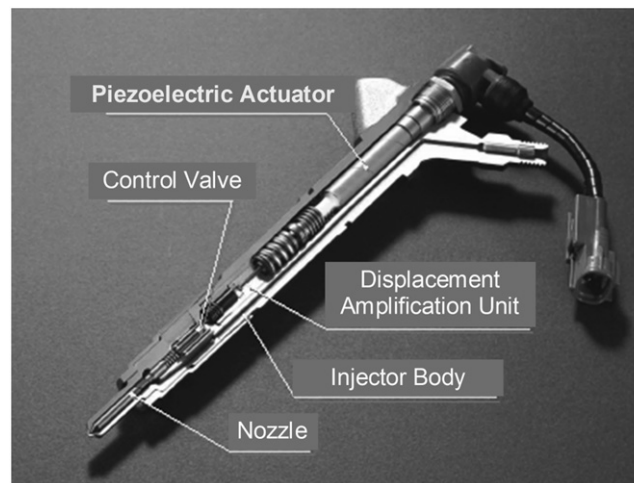


Fig. 24 Common rail type diesel injection valve with a piezoelectric multilayer actuator. Courtesy by Denso Corporation.

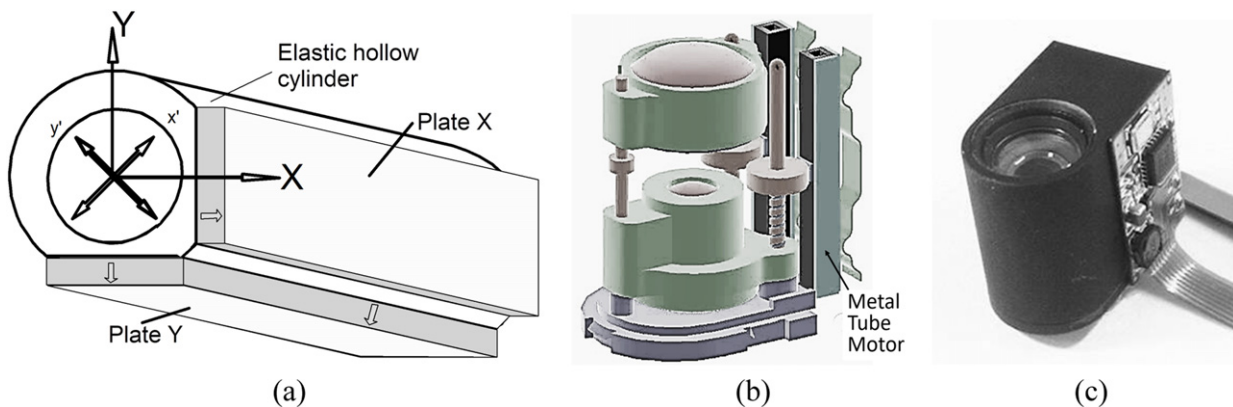


Fig. 25 (a) Structure of a "Metal tube" motor using a metal tube and two rectangular PZT plates. (b) Structure of the camera auto zooming/focusing mechanism with two metal tube USM's. (c) Photo of the camera module in a Samsung cellular phone.

Our application target of the 'Cymbal' was set to hybrid vehicles with both an engine and an electromagnetic motor, in collaboration with Toyota Central Research Labs; (1) reducing the engine vibration and (2) harvesting electric energy (~ 1 W) to car batteries to increase the mileage. A cymbal with 29 mm diameter and 1 $\sim$ 2 mm thick (0.3 mm thick stainless steel end caps), 9 pieces of which are to be inserted below a 40 kg engine weight (400 N bias force), was shaken under an electromagnetic shaker (in experiment) at 100 Hz, which generated 80 mW electric power (Kim *et al.*, 2004, 2005). 9 cymbals embedded in engine damper rubber sheets could provide the total electric power level close to 1 W to a car battery.

We should also point out here that there is another research category of piezo-energy harvesting; that is, small energy harvesting (mW) for signal transfer applications, where the efficiency is not a primary objective. This category usually treats an impulse/snap action load to generate instantaneous electric energy for transmitting signals for a short period (100 ms $\sim$ 10 s), without accumulating the electricity in a rechargeable battery. NEC-Tokin developed an LED traffic light array system driven by a piezoelectric windmill (Uchino, 2010), which is operated by wind generated effectively by passing automobiles. Successful million selling products in the commercial market belong mostly to this category at present, including 'Lightning Switch' see "Relevant Websites section" and the 25 mm caliber 'Programmable Ammunition' see "Relevant Websites section". The former by PulseSwitch Systems, VA is a remote switch for room lights, with using a unimorph piezoelectric component (Fig. 26(a)). In addition to the living convenience, Lightning Switch can reduce the housing construction cost drastically, due to a significant reduction of the copper electric wire and the aligning labor. To the contrary, the 25-mm caliber 'Programmable Ammunition' see "Relevant Websites section" is based on electricity generation with a multilayer piezo-actuator under shot impact to maneuver the bullet via an operational amplifier, developed by Micromechatronics Inc., PA and ATK Integrated Weapon Systems, AZ (Fig. 26(b)). A piezo energy harvesting device was installed because the original button battery was decayed in two months under high temperature atmosphere in the Afghanistan battle field.

Though relatively large investments and research efforts are being put on MEMS/NEMS and 'nano harvesting' devices, the development strategy change is mandatorily required, except for the sensor applications. Even for medical applications, obtained/

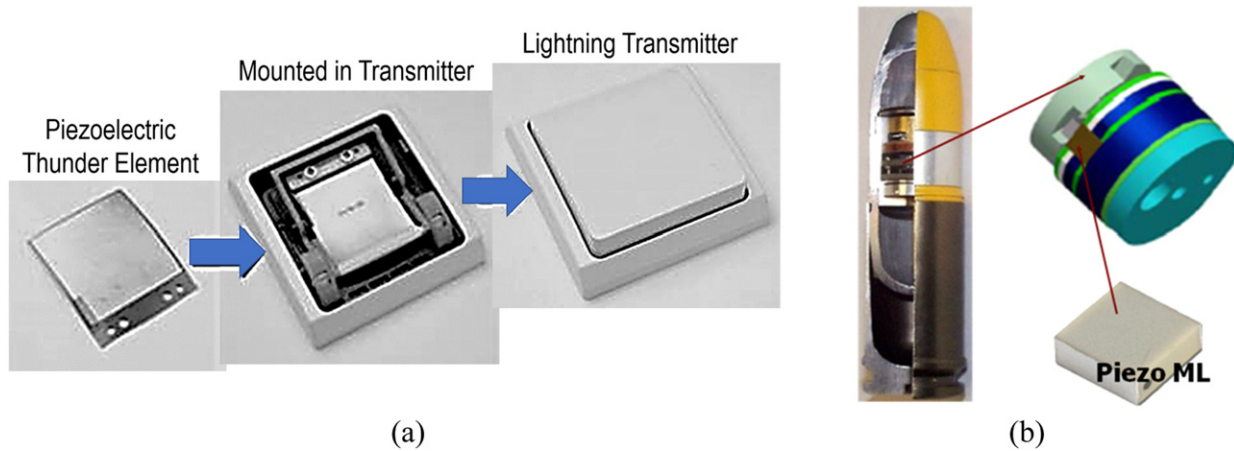


Fig. 26 (a) Lightning Switch with piezoelectric Thunder actuator (Courtesy by Face Electronics). (b) Programmable air-burst munition (PABM, 25 mm caliber) developed by Micromechatronics. (Courtesy by Face Electronics).

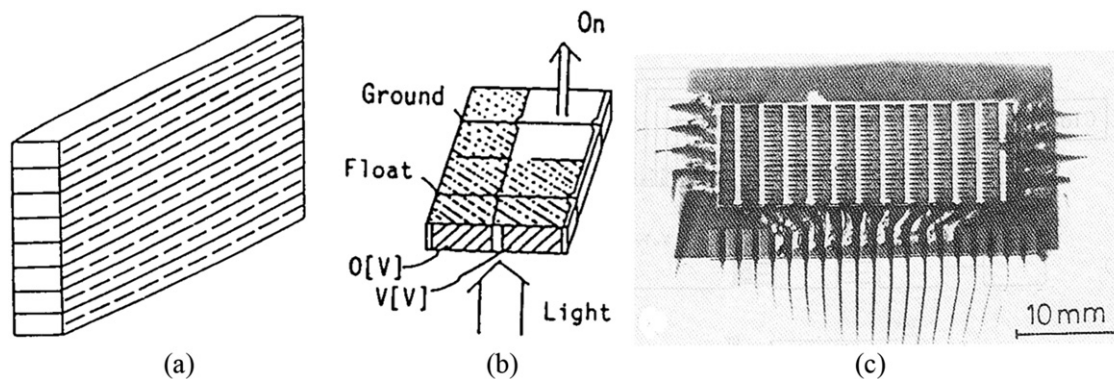


Fig. 27 A 2D PLZT optical display: (a) a matrix segment and (b) detail of an activated portion of the display. (c) top view photograph of a PLZT light valve array with external electrodes.

reported energy level $\text{pW} \sim \text{nW}$ from one component (this level is called 'sensor', not 'energy harvester', in practice) is a useless level, which is originated from inevitable small volume of the used piezoelectric material (i.e., $1 \mu\text{m}$ thin films). Note that minimum 1 mm^3 PZT is required for generating a couple of mW (as long as we use the current PZT materials), minimum level for the most of energy harvesting applications. If we can find a particular application which requires only $1 \mu\text{W}$ electric energy (the author does not know many), the commercialization effort should be necessary. Otherwise, "Nano-grid" researches to reach to minimum 1 mW level by connecting thousands of nano-harvesting devices, is highly encouraged, rather than merely the MEMS fabrication process from an academic viewpoint. Also, the development should be shifted on thick PZT films 30–50 μm in order to reach 1 mW energy generation from one component (Uchino, 2021).

Two-Dimensional Displays

We introduce the 2D display development effort conducted by Fujitsu General, Japan in collaboration with the author's group in the late 1980s, because it is sophisticated in design and applicability even for the future applications (Uchino *et al.*, 1990). The original motivation was to develop projection-type high-definition TVs then, competing with liquid crystal displays.

The structure for the 2D PLZT light valve array is shown in Fig. 27(a), (b) and (c), (Uchino *et al.*, 1990) which were prepared by the green-sheet multilayer (ML) technology, aiming as mass-production. Coprecipitated PLZT 9/65/35 (Kerr effect composition) powders were mixed with organic solvent and binder and formed into a green sheet. Platinum internal electrodes were printed on the green sheets. The electroded sheets were then laminated, with the electrodes alternating by 90° between sheets, under a pressure of 3000 psi. The laminated body was sintered in an oxygen-controlled atmosphere, and the bulk was cut and polished. Finally the external electrodes were applied for vertical and horizontal addressing for individual pixels on the display, as shown in Fig. 27(c).

Fig. 27(b) shows the detailed electrode configuration of an arrayed light valve. The unshaded portion of the device (a pair of segments sandwiching horizontal “Ground” electrode) in the figure represents one image unit (pixel), on/off control of which is made by addressing “horizontal ground” and “vertical high-voltage (V)”. The separated internal electrodes are connected by vertical external electrodes printed on the surface of the device (see **Fig. 27(c)**). The continuous (plate-through) horizontal electrodes are embedded 100 μm below the optical surface to avoid shorting with the surface vertical electrodes connecting the separated internal electrodes. **Fig. 27(c)** shows a photo of an actual display. Note that the PLZT layer thickness is about 0.35 mm (Uchino *et al.*, 1990).

Advantages of the PLZT display compared to the LCD display include: (1) much faster response speed less than 10 μs , (2) durability to environmental high temperature, and (3) mass-production capability and inexpensive manufacturing cost, comparable to the LCD. Because of these superior performances, future applications in conjunction with the computer technology such as “neural network computers” are highly anticipated, rather than commercial TVs.

Conclusions

Ferroelectric materials, especially polycrystalline ceramics, are very promising for a variety of applications such as (1) high permittivity capacitors, (2) ferroelectric memories, (3) pyroelectric sensors and electrocaloric refrigerators, (4) piezoelectric and electrostrictive transducers, (5) electrooptic devices and (6) PTC thermistors. As a concluding remark, the author points out five key trends for providing the future perspectives of ferroelectric devices; “Performance to Reliability” (Pb-free piezoelectrics, bio-degradable piezo-polymer, low loss piezoelectric), “Hard to Soft” (foldable piezo-polymer film, elastically compliant PMN/PZN single crystals), “Macro to Nano” (piezo-MEMS), “Homo to Hetero” (flexoelectricity, monomorph) and “Single to Multi-functional” (magnetoelectrics, photostriction). In the application area, the global regime for “ecological sustainability” particularly accelerated new developments in ultrasonic disposal technology of hazardous materials, diesel injection valves for air pollution, and piezoelectric renewable energy harvesting systems. Refer to Uchino (2014) for further information.

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New Scale Technologies, 121 Victor Heights Parkway, Victor, NY 14564.

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MarkLines Co., Ltd., 2-11-1 Nagatacho, Chiyoda-Ku, Tokyo, Japan.

High Power Piezoelectric Materials

K Uchino, Electrical Engineering, The Penn State University, State College, PA, United States

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Abstract

Heat generation is one of the significant problems in piezoelectrics for high-power density applications. In this article, we review the loss phenomenology in piezoelectrics first, including three losses, dielectric, elastic and piezoelectric losses, followed by heat generation analysis in piezoelectric materials for pseudo-DC and AC drive conditions. Heat generation at off-resonance is attributed mainly to intensive dielectric loss $\tan\delta$, while the heat generation at resonance is mainly originated from the intensive elastic loss $\tan\phi$. Third, various experimental techniques (High Power Characterization System, HiPoCS) are introduced to measure dielectric, elastic and piezoelectric losses separately, including admittance/impedance spectrum analysis and burst/transient response method. Mechanical quality factors (Q_A at resonance and Q_B at antiresonance) are primarily measured as a function of vibration velocity. Fourth, loss mechanisms are discussed from the materials science viewpoint, in particular, from the domain dynamics models. The polarization angle dependence of losses in PZT's and crystallographic orientation dependence of PMN-PT single crystal losses provide insightful domain dynamic models, including negative extensive piezoelectric loss $\tan\theta$. Then, practical high power "hard $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT)" based materials are described from four approaches: (1) ionic doping (acceptor doping creates hard PZTs), (2) material's composition (higher Curie temperature ferroelectrics exhibit higher coercive field in general), (3) Pb-free piezoelectrics (crystallographic difference and lower thermal conductivity helps higher power density), and (4) grain size control (smaller grain specimens exhibit higher maximum vibration velocity). Piezo-ceramics with the maximum vibration velocities close to 1 m/s (rms) are now available, which lead to the power density capability 10 times that of the commercially available hard PZTs. We proposed an "internal bias field model" to explain the low loss and high-power origin of these materials. Finally, we also introduce DC bias electric field and stress dependence of losses from the practical specimen driving technique viewpoint for the high-power applications.

Key Points

- Learn the heat generation and loss mechanisms in piezoelectrics in order to obtain the development strategies of high-power density piezoelectrics.
- Learn the origin of the mechanical quality factor of a piezo-component of a particular configuration at the resonance and antiresonance frequencies for determining the optimal drive frequency for minimizing the input electric power.
- Learn "High Power Piezoelectric Characterization System (HiPoCS)".
- Strategy how to develop high-power piezoelectric ceramics; hard PZTs.
- Polarization angle dependence of losses (sample geometry) from the high-power application viewpoints for obtaining the insight on the domain wall dynamics.
- DC bias stress and electric field dependence of losses (sample driving technique) from the high-power application viewpoints; such as Langevin transducers.

Introduction

This article reviews first the loss phenomenology in piezoelectrics, including three losses, dielectric, elastic and piezoelectric losses, followed by heat generation analysis in piezoelectric materials for pseudo-DC and AC drive conditions. Third, various experimental techniques (High Power Characterization System, HiPoCS) are introduced to measure dielectric, elastic and piezoelectric losses separately, including admittance/impedance spectrum analysis and burst/transient response method. Mechanical quality factors (Q_A at resonance and Q_B at antiresonance) are primarily measured as a function of vibration velocity. Fourth, loss mechanisms are discussed, in particular, from the domain dynamics models. The polarization angle dependence of losses in PZT's and crystallographic orientation dependence of PMN-PT single crystal losses provide insightful domain dynamic models, including negative extensive piezoelectric loss $\tan\theta$. Then, practical high-power "hard $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT)" based materials are described, which exhibit vibration velocities close to 1 m/s (rms). Finally, we also introduce the DC bias electric field and stress dependence of losses from the specimen driving technique viewpoint for the high-power applications. "High-Power Piezoelectrics and Loss Mechanisms", CRC Press (2020) (Uchino, 2020a).

Background of High-Power Piezoelectrics

With accelerating the commercialization of piezoelectric actuators and transducers for portable equipment applications, we identified the bottleneck of the piezoelectric devices; that is, significant "heat generation" limits the maximum power density. The current maximum handling power density of a commercially-available hard $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) is only around 5 W/cm³ at present.

We desire 100 W/cm^3 or higher power density for further miniaturization of devices (such as piezo MEMS actuators) without losing efficiency. Thus, the main research focus seems to be shifting from the “real parameters” such as larger polarization and displacement, to the “imaginary parameters” such as polarization/displacement hysteresis, heat generation, and mechanical quality factor, which are originated from three loss factors (dielectric, elastic, and piezoelectric losses). Reducing hysteresis and heat generation, then increasing the mechanical quality factor to amplify the resonance displacement are the primary targets. However, since the resonance displacement is provided by a product of the “mechanical quality factor Q_m ” and the real parameter piezoelectric constant d , and the Q_m value is usually reduced with increasing d in the piezoceramics, the target of the material development is highly complicated.

Loss and hysteresis in piezoelectrics exhibit both merits and demerits in general. For positioning actuator applications, hysteresis in the field-induced strain causes a serious problem, and for resonance actuators such as ultrasonic motors, loss generates significant heat in the piezoelectric materials. Further, in consideration of the resonant strain amplified in proportion to the Q_m , low (intensive) mechanical loss materials are preferred for ultrasonic motors. In contrast, for force sensors, acoustic transducers and piezoelectric energy harvesting systems, a low mechanical quality factor Q_m (which corresponds to high mechanical loss) is essential in order to widen a frequency range for receiving signals. In summary, this article focuses on “high-power actuator developments”, not on sensor applications.

Historically, Haerdtl wrote a review article on electrical and mechanical losses in ferroelectric ceramics in the early 1980s (Haerdtl, 1982). Losses are considered to consist of four portions: (1) domain wall motion, (2) fundamental lattice portion, which should also occur in domain-free monocrystals, (3) microstructure portion, which occurs typically in polycrystalline samples, and (4) conductivity portion in highly-ohmic samples. However, because in the typical piezoelectric ceramic (i.e., polycrystalline) case, the loss due to the domain wall motion exceeds the other three contributions significantly, this article focuses on the domain wall dynamics for the loss origin. Not many systematic studies of the loss mechanisms in piezoelectrics have been reported, particularly in high electric field and high-power density ranges. Although part of the formulas of this manuscript was described by Ikeda in his textbook (Ikeda, 1984), the “piezoelectric losses”, which have been found in our investigations to play an important role, were neglected then. “Equivalent circuit analyses” as a simple method have been adopted by various researchers to consider the electrical behavior, including “losses” (Seo *et al.*, 2005; de Paco *et al.*, 2008; Lin, 2010; Smyth and Kim, 2015; Nakamoto and Moriizumi, 1990; Krauss *et al.*, 1994; Chen *et al.*, 1997; Arnold and Muhlen, 2003; Sun *et al.*, 2014). For example, the Mason’s equivalent circuit was derived from the piezoelectric constitutive and motion equations, therefore, the electro-mechanical conversion process is clearly described. Though there exist three fundamental losses in the piezoelectric materials (dielectric, elastic and piezoelectric losses), equivalent circuits so far reported included the mechanical/elastic loss factor (and dielectric loss, occasionally) on the basis of the Mason’s model (Budinger *et al.*, 2004; Zhou *et al.*, 2011; Lin *et al.*, 2016). Damjanovic proposed an equivalent circuit to present the influence of the piezoelectric loss (Damjanovic, 1990), while the coupled loss formulas were insufficient to measure three losses separately in piezoelectric materials. The major problem is found even in the present IEEE Standard on Piezoelectricity, (ANSI/IEEE Std 176–1987, 1987). This Standard does not include the terminology, “piezoelectric loss”, nor discuss the difference of mechanical quality factors Q_A (at resonance) and Q_B (at antiresonance); that is, both are exactly the same, against many of the practical experimental results and reports (ANSI/IEEE Std 176–1987, 1987; Setter, 2002).

Being motivated by various engineers’ requests, the author elucidates the comprehensive researches on piezoelectric losses in this article. We review first the loss phenomenology in piezoelectrics, including three losses, dielectric, elastic and piezoelectric losses, followed by heat generation analysis in piezoelectric materials for pseudo-DC and AC drive conditions. Third, various experimental techniques (High Power Characterization System, HiPoCS) are introduced to measure dielectric, elastic and piezoelectric losses separately, including admittance/impedance spectrum analysis and burst/transient response method. Mechanical quality factors (Q_A at resonance and Q_B at antiresonance) are primarily measured as a function of vibration velocity. Fourth, loss mechanisms are discussed, in particular, from the domain dynamics models. The polarization angle dependence of losses in PZT’s and crystallographic orientation dependence of PMN-PT single crystal losses provide insightful domain dynamic models, including negative extensive piezoelectric loss $\tan\theta$. Then, practical high-power “hard $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT)” based materials are described, which exhibit vibration velocities close to 1 m/s (rms). Finally, we also introduce the DC bias electric field and stress dependence of losses from the practical specimen driving technique viewpoint for the high-power applications.

The terminologies, “intensive” and “extensive” losses are introduced in my discussion, in the relation with “intensive” and “extensive” parameters in the phenomenology. Suppose a certain volume of material first, then imagine to cut it half. Extensive parameter (material’s internal parameter such as displacement L /strain x and total dipole moment/electric displacement D) depends on the volume of the material (i.e., becomes a half), while the intensive parameter (externally controllable parameter such as force F /stress X and electric field E) is independent on the volume of the material. These are not related with the “intrinsic” and “extrinsic” losses which were introduced to explain the loss contribution from the mono-domain single crystal state and the others (Setter, 2002). It is important to note that “extensive (or intensive) loss” should be understood just as an abbreviation of the “loss associated with extensive (or intensive) parameter”; that is, the extensive loss does not become a half even the specimen is cut into half, because the loss factor is already normalized in terms of the real extensive parameter. The experimentally obtained losses are mostly “intensive losses”, while “extensive losses” are focused in our discussion on domain dynamics in piezoelectrics. However, remember that physical parameters of their performance such as permittivity and elastic compliance still differ in piezoelectric materials, depending on the boundary conditions; mechanically free or clamped, and electrically short-circuit or open-circuit. These are also distinguished as “intensive” or “extensive” parameters and their associated losses.

Phenomenological Approach to Losses in Piezoelectrics

Piezoelectric Constitutive Equations

Intensive losses

Since the detailed mathematical treatment has been described in a previous paper (Hirose *et al.*, 1996), we summarize the essential results in this section. We start from the following two “piezoelectric constitutive equations”:

$$x = s^E X + dE, \quad (1)$$

$$D = dX + \varepsilon_0 \varepsilon^X E, \quad (2)$$

where, x is strain, X , stress, D , electric displacement, E , electric field. Eqs. (1) and (2) are expressed in terms of “intensive” (i.e., externally controllable) physical parameters X and E . The elastic compliance s^E , the dielectric constant ε^X and the piezoelectric constant d are temperature-dependent in general. Note that the piezoelectric constitutive equations cannot yield a delay-time related loss, in general, without considering “irreversible thermodynamic equations” or “dissipation functions”. However, the dissipation functions are mathematically equivalent to the introduction of “complex physical constants” into the phenomenological equations, if the loss is small and can be treated as a perturbation (“dissipation factor tangent” $\ll 0.1$). Therefore, we will introduce complex parameters ε^{X*} , s^{E*} and d^* , using $*$, in order to consider the small hysteresis losses in dielectric, elastic and piezoelectric constants:

$$\varepsilon^{X*} = \varepsilon^X (1 - j \tan \delta'), \quad (3)$$

$$s^{E*} = s^E (1 - j \tan \phi'), \quad (4)$$

$$d^* = d (1 - j \tan \theta'). \quad (5)$$

θ' is the phase delay of the strain under an applied electric field, or the phase delay of the electric displacement under applied stress. Both phase delays should be exactly the same if we introduce the same complex piezoelectric constant d^* into Eqs. (1) and (2). δ' is the phase delay of the electric displacement to an applied electric field under a constant stress (e.g., zero stress) condition, and ϕ' is the phase delay of the strain to applied stress under a constant electric field (e.g., short-circuit) condition. We will consider these phase delays with prime as “intensive losses”.

Fig. 1(a)–(d) correspond to the model hysteresis curves for practical experiments: D (or P in practice in high permittivity ferroelectrics) versus E curve under a stress-free condition, x versus X under a short-circuit condition, x versus E under a stress-free condition and D versus X under a short-circuit condition for measuring current, respectively. Note that these measurements are easily conducted. The average slope of the D - E hysteresis curve in Fig. 1(a) corresponds to the permittivity $\varepsilon^X_{E_0}$, where the superscript stands for $X = \text{constant}$ (occasionally zero). Thus, $\tan \delta'$ is called “an intensive dielectric loss tangent”. The situation of s^E is similar; the slope of the x - X relation is the elastic compliance under $E = \text{constant}$ condition.

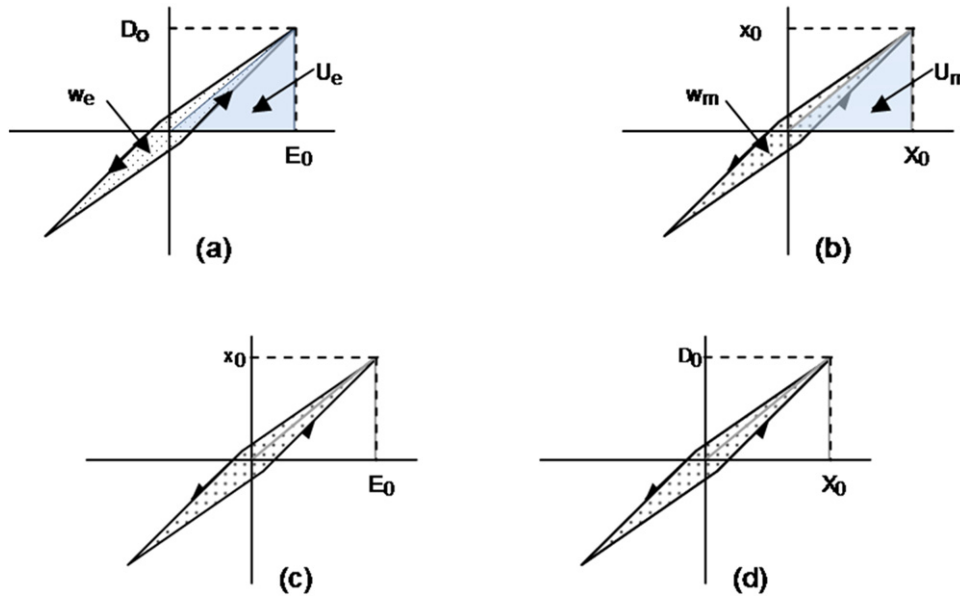


Fig. 1 (a) D versus E (stress free), (b) x versus X (short-circuit), (c) x versus E (stress free) and (d) D versus X (short-circuit) curves with a slight hysteresis in each relation.

Since the areas on the D - E and x - X domains exhibit directly the electrical and mechanical energies, respectively (see Fig. 1(a) and (b)), the stored energies (during a quarter cycle) and hysteresis losses (during a full electric or stress cycle) for pure dielectric and elastic energies can be calculated as:

$$U_e = (1/2)\epsilon_0\epsilon^X E_0^2, \quad (6a)$$

$$w_e = \pi\epsilon_0\epsilon^X E_0^2 \tan\delta', \quad (6b)$$

$$U_m = (1/2)s^E X_0^2, \quad (7a)$$

$$w_m = \pi s^E X_0^2 \tan\phi'. \quad (7b)$$

The dissipation factors, $\tan\delta'$ and $\tan\phi'$, can be experimentally obtained by measuring the dotted hysteresis area and the stored energy area; that is, $(1/2\pi)(w_e/U_e)$ and $(1/2\pi)(w_m/U_m)$, respectively. Note that the factor (2π) comes from the integral per cycle. The electromechanical hysteresis loss calculations, however, are more complicated, because the areas on the x - E and P - X domains do not directly provide energy. The areas on these domains can be calculated as follows, depending on the measuring ways; when measuring the induced strain under an electric field, the electro-mechanical conversion energy can be calculated as follows, by converting E to stress X :

$$U_{em} = \int x dX = \left(\frac{1}{s^E}\right) \int x dx = (d^2/s^E) \int_0^{E_0} E dE = \left(\frac{1}{2}\right)(d^2/s^E) E_0^2, \quad (8a)$$

where $x = dE$ was used. Then, using Eqs. (4) and (5), and from the imaginary part, we obtain the loss during a full cycle as

$$w_{em} = \pi(d^2/s^E) E_0^2 (2\tan\theta' - \tan\phi'). \quad (8b)$$

Note that the area ratio in the strain *versus* electric field measurement should provide the combination of piezoelectric loss $\tan\theta'$ and elastic loss $\tan\phi'$ (not $\tan\theta'$ directly!). When we measure the induced charge under stress, the stored energy U_{me} and the hysteresis loss w_{me} during a quarter and a full stress cycle, respectively, are obtained similarly as

$$U_{me} = \int D dE = \left(\frac{1}{2}\right)(d^2/\epsilon_0\epsilon^X) X_0^2, \quad (9a)$$

$$w_{me} = \pi(d^2/\epsilon_0\epsilon^X) X_0^2 (2\tan\theta' - \tan\delta'). \quad (9b)$$

Now, the area ratio in the charge versus stress measurement provides the combination of piezoelectric loss $\tan\theta'$ and dielectric loss $\tan\delta'$. Hence, from the measurements of D versus E and x versus X , we obtain $\tan\delta'$ and $\tan\phi'$, respectively, and either the piezoelectric (D versus X) or converse piezoelectric measurement (x versus E) provides $\tan\theta'$ through a numerical subtraction. The above equations provide a traditional loss measuring technique on piezoelectric actuators, an example of which is introduced in Section "High Power Piezoelectric Characterization System (HiPoCS)".

Extensive losses

In order to consider the physical meanings of the losses in the material (e.g., domain dynamics), we will introduce the "extensive losses" (Hirose *et al.*, 1996) in terms of "extensive parameters" x and D . In practice, intensive losses are easily measurable, but extensive losses are not in the pseudo-DC measurement, but obtainable from the intensive losses by using the "K-matrix" introduced later. When we start from the piezoelectric equations in terms of extensive physical parameters x and D ,

$$X = c^D x - hD, \quad (10)$$

$$E = -hx + \kappa^X \kappa_0 D, \quad (11)$$

where c^D is the elastic stiffness under $D = \text{constant}$ condition (i.e., electrically open-circuit), κ^X is the inverse dielectric constant under $x = \text{constant}$ condition (i.e., mechanically clamped) and h is the inverse piezoelectric constant d . We introduce the "extensive dielectric, elastic and piezoelectric losses" as

$$\kappa^{X*} = \kappa^X (1 + j\tan\delta), \quad (12)$$

$$c^{D*} = c^D (1 + j\tan\phi), \quad (13)$$

$$h^* = h(1 + j\tan\theta). \quad (14)$$

We denote these phase delays with non-prime as "extensive losses". The sign "+" in front of the imaginary " j " is taken by a general induction principle; that is "polarization induced after electric field application" and so on. However, regarding the extensive piezoelectric loss $\tan\theta$, we do not know the sign empirically [We observed negative $\tan\theta$ in Section "Dc Bias Electric Field & Stress Effect On Losses"]. It is notable that the permittivity under a constant strain (e.g., zero strain or completely clamped) condition, ϵ^{X*} and the elastic compliance under a constant electric displacement (e.g., open-circuit) condition, s^{D*} can be provided as an inverse value of κ^{X*} and c^{D*} , respectively, in this simplest 1-D expression. Thus, using exactly the same losses in Eqs. (16) and (17),

$$\varepsilon^{x*} = \varepsilon^x (1 - j \tan \delta), \quad (15)$$

$$s^{D*} = s^D (1 - j \tan \phi), \quad (16)$$

We will consider these phase delays again as “extensive losses”. Care should be taken in the case of a general 3-D expression, where this part must be translated as “inverse” matrix components of κ^{x*} and c^{D*} tensors.

Electromechanical Coupling Factor

The term, “electromechanical coupling factor” k , is defined as the square value k^2 being the ratio of the converted energy over the input energy: when electric to mechanical

$$k^2 = (\text{Stored mechanical energy} / \text{Input electrical energy}), \quad (17a)$$

or when mechanical to electric,

$$k^2 = (\text{Stored electrical energy} / \text{Input mechanical energy}) \quad (17b)$$

Let us derive Eq. (17a) first practically, when an external electric field E_3 is applied to a piezoelectric material in a pseudo-static process. See Fig. 2(a), when we apply an electric field on the top and bottom electrodes under stress free condition ($X = 0$). Input electric energy must be equal to $(1/2)\varepsilon_0 \varepsilon_3^X E_3^2$ and the output strain generated by E_3 should be $d_{33} E_3$. Since the converted/stored mechanical energy is obtained as $(1/2)s_{33}^E x_3^2$, we obtain:

$$\begin{aligned} k_{33}^2 &= [(1/2)(d_{33} E_3)^2 / s_{33}^E] / [(1/2)\varepsilon_0 \varepsilon_3^X E_3^2] \\ &= d_{33}^2 / \varepsilon_0 \varepsilon_3^X s_{33}^E. \end{aligned} \quad (18a)$$

Let us now consider Eq. (17b), when an external stress X_3 is applied to a piezoelectric material in a pseudo-static process in Fig. 2(b). Using a similar derivation process:

$$\begin{aligned} k_{33}^2 &= [(1/2\varepsilon_0 \varepsilon_3^X)(d_{33} X_3)^2] / [(1/2)s_{33}^E X_3^2] \\ &= d_{33}^2 / \varepsilon_0 \varepsilon_3^X s_{33}^E. \end{aligned} \quad (18b)$$

It is essential to understand that the electromechanical coupling factor k or k^2 (energy transduction or conversion rate) can be exactly the same for both converse (17a) and direct (17b) piezoelectric effects. The conditions under constant X (free stress) or constant E (short-circuit) are considered to be unconstrained. If you conduct an analogous discussion on the extensive constitutive equations Eqs. (10) and (11), you obtain the following relation on the electromechanical coupling factor k :

$$k^2 = d^2 / (s^E \varepsilon_0 \varepsilon^X) = h^2 / (c^D \kappa_0 \kappa^X). \quad (19)$$

The electromechanical coupling factor is a real number under a pseudo-static condition; while under a dynamic condition, taking into account the time lag, it can be a complex parameter as

$$k^{2*} = k^2 [1 - (2 \tan \theta' - \tan \delta' - \tan \phi')] = k^2 [1 + (2 \tan \theta - \tan \delta - \tan \phi)] \quad (20)$$

Constraint Physical Parameters – Permittivity/Elastic Compliance and Related Losses

Here, we consider the physical property change with the boundary conditions: E constant/ D constant, or X constant/ x constant in a simplest 1-D model. When an electric field is applied to a piezoelectric specimen as illustrated in the top part of Fig. 3, this state will be equivalent to the superposition of the following two steps: first, the sample is completely clamped and the field E_0 is applied (pure electrical energy $(\frac{1}{2})\varepsilon_0 \varepsilon^X E_0^2$ is input); second, keeping the field at E_0 , the mechanical constraint is released (additional mechanical energy

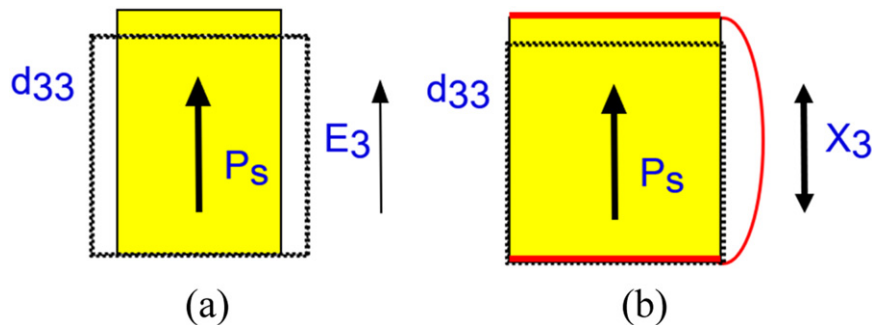


Fig. 2 Calculation models of electro-mechanical coupling factor k for (a) electric input under stress free, and (b) stress input under short-circuit condition.

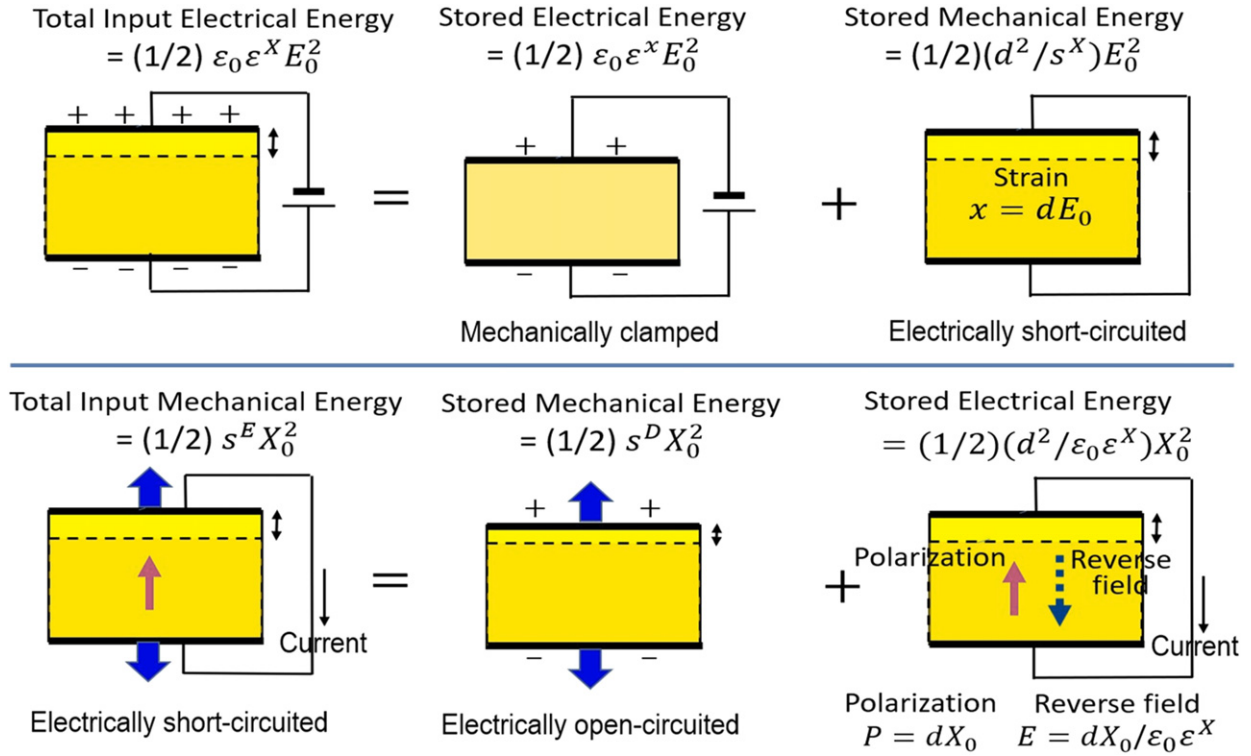


Fig. 3 Conceptual figure for explaining the relation between ϵ^X and ϵ^E , s^E and s^D .

($\frac{1}{2}x^2/s^E = (\frac{1}{2})(d^2/s^E)E_0^2$ is necessary). The total energy should correspond to the total input electrical energy ($\frac{1}{2}\epsilon_0\epsilon^XE_0^2$ under stress free condition (left figure). That is, $(\frac{1}{2})\epsilon_0\epsilon^XE_0^2 = (\frac{1}{2})\epsilon_0\epsilon^XE_0^2 + (\frac{1}{2})(d^2/s^E)E_0^2$. Similar energy calculation can be obtained from the bottom part of **Fig. 3**, leading to the following equations:

$$\epsilon^X/\epsilon^E = (1 - k^2), \quad (21)$$

$$s^D/s^E = (1 - k^2). \quad (22)$$

Similar relations are obtained for the extensive constitutive equations:

$$\kappa^X/\kappa^E = (1 - k^2), \quad (23)$$

$$c^E/c^D = (1 - k^2), \quad (24)$$

It is noteworthy that k in the above Eqs. (21)–(24) is called the “electromechanical coupling factor” defined by $k^2 = d^2/(s^E\epsilon_0\epsilon^X) = h^2/(c^D\kappa_0\kappa^X)$.

In order to obtain the relationships between the intensive and extensive losses, the following three equations are essential:

$$\epsilon_0\epsilon^X = [\kappa_0\kappa^X(1 - h^2/(c^D\kappa_0\kappa^X))]^{-1}, \quad (25)$$

$$s^E = [c^D(1 - h^2/(c^D\kappa_0\kappa^X))]^{-1}, \quad (26)$$

$$d = [h^2/(c^D\kappa_0\kappa^X)][h(1 - h^2/(c^D\kappa_0\kappa^X))]^{-1}. \quad (27)$$

Replacing the parameters in Eqs. (25)–(27) by the complex parameters in Eqs. (3)–(5), (12)–(14), we obtain the relationships between the intensive and extensive losses:

$$\tan\delta' = (1/(1 - k^2))[\tan\delta + k^2(\tan\phi - 2\tan\theta)], \quad (28)$$

$$\tan\phi' = (1/(1 - k^2))[\tan\phi + k^2(\tan\delta - 2\tan\theta)], \quad (29)$$

$$\tan\theta' = (1/(1 - k^2))[\tan\delta + \tan\phi - (1 + k^2)\tan\theta], \quad (30)$$

where k is the electromechanical coupling factor defined by Eq. (19), and here as a real number. It is important that the intensive dielectric, elastic and piezoelectric losses (with prime) are mutually correlated with the extensive dielectric, elastic and piezoelectric losses (non-prime) through the electromechanical coupling k^2 , and that the denominator $(1 - k^2)$ comes basically from the ratios, $\epsilon^X/\epsilon^E = (1 - k^2)$ and $s^D/s^E = (1 - k^2)$, and this real part reflects to the dissipation factor when the imaginary part is

divided by the real part. Knowing the relationships between the intensive and extensive physical parameters, and the electro-mechanical coupling factor k , the intensive (prime) and extensive (non-prime) loss factors have the following relationship:

$$\begin{bmatrix} \tan\delta' \\ \tan\phi' \\ \tan\theta' \end{bmatrix} = [K] \begin{bmatrix} \tan\delta \\ \tan\phi \\ \tan\theta \end{bmatrix}, \text{ or } \begin{bmatrix} \tan\delta \\ \tan\phi \\ \tan\theta \end{bmatrix} = [K] \begin{bmatrix} \tan\delta' \\ \tan\phi' \\ \tan\theta' \end{bmatrix} \quad (31a)$$

$$[K] = \frac{1}{1-k^2} \begin{bmatrix} 1 & k^2 & -2k^2 \\ k^2 & 1 & -2k^2 \\ 1 & 1 & -1-k^2 \end{bmatrix}, \quad \left[k^2 = \frac{d^2}{s^E(\epsilon_0\epsilon^X)} = \frac{h^2}{c^D(\kappa_0\kappa^X)} \right] \quad (31b)$$

The matrix $[K]$ is proven to be “invertible”; that is, $K^2 = I$, or $K = K^{-1}$, where I is the identity matrix. Hence the conversion relationship between the intensive (prime) and extensive (non-prime) exhibits full symmetry. The author emphasizes again that the extensive losses are more important for considering the physical micro/macrosopic models, and can be obtained mathematically from a set of intensive losses, which can be obtained more easily from the experiments.

In the case of a 3-D expression, a PZT polycrystalline ceramic (∞mm) holds 10 tensor components, as given below [note $s_{66} = 2(s_{11} - s_{12})$ in the ∞ symmetry]:

$$\begin{bmatrix} s_{11}^* & s_{12}^* & s_{13}^* & 0 & 0 & 0 \\ s_{12}^* & s_{11}^* & s_{13}^* & 0 & 0 & 0 \\ s_{13}^* & s_{13}^* & s_{33}^* & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44}^* & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{44}^* & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{66}^* \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15}^* & 0 \\ 0 & 0 & 0 & d_{15}^* & 0 & 0 \\ d_{31}^* & d_{31}^* & d_{33}^* & 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} \epsilon_{11}^* & 0 & 0 \\ 0 & \epsilon_{11}^* & 0 \\ 0 & 0 & \epsilon_{33}^* \end{bmatrix},$$

where * means a complex parameter, leading to 20 loss tensor components, taking into account both intensive and extensive losses. However, only 10 components are independent, because of the relationship between the intensive and extensive losses given by Eqs. (31a) and (31b).

Piezoelectric Resonance and Antiresonance

So far our discussion is primarily made under a pseudo static condition. When the field E or external stress X is alternating, mechanical vibration is caused in a piezoelectric specimen. If the drive frequency is adjusted to its mechanical resonance frequency of the piezoelectric specimen, the vibrating displacement is significantly amplified with nonuniform stress distribution in a specimen. This phenomenon can be understood as a strain amplification due to synchronous accumulation of the input electric energy with time (“amplification in terms of time”), which is called “piezoelectric resonance”. The amplification factor is proportional to the mechanical quality factor Q_m (inversely proportional to the elastic loss). Piezoelectric resonance is very useful for realizing energy trap devices, filters, actuators, medical and underwater transducers, piezo-transformers etc. We consider in this section the electromechanical resonance under an AC external electric field theoretically. We also introduce the difference of the “mechanical quality factor” Q_m at the resonance and antiresonance frequencies by integrating three losses (i.e., dielectric, elastic and piezoelectric losses).

Longitudinal vibration analysis – k_{31} type

Let us consider the longitudinal mechanical vibration of a piezoceramic plate through the transverse piezoelectric effect (d_{31}), as shown in Fig. 4. Sinusoidal electric field E_z (angular frequency ω) is applied along the polarization P_z direction. If the polarization is in the z -direction and x - y top and bottom planes are the planes of the electrodes, the extensional vibration in the x (length) direction is represented by the following dynamic equations (when the length L is more than 4–6 times of the width w or the thickness b , we can neglect the coupling modes with width or thickness vibrations):

$$\rho \frac{\partial^2 u}{\partial t^2} = F = \frac{\partial X_{11}}{\partial x} + \frac{\partial X_{12}}{\partial y} + \frac{\partial X_{13}}{\partial z}, \quad (32)$$

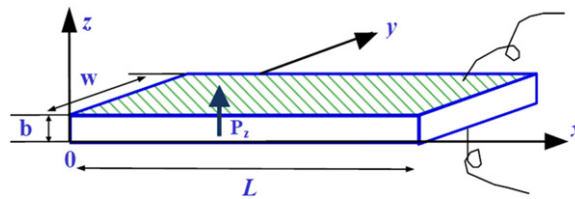


Fig. 4 Longitudinal vibration through the transverse piezoelectric effect (d_{31}) in a rectangular plate ($L \gg w \gg b$).

where ρ is the density of the piezo-ceramic, u is the displacement of a small volume element in the ceramic plate in the x -direction.

We integrate the following “intensive piezoelectric constitutive equations” into the dynamic equation:

(1) $x = dE + s^E X$, and (2) $D = \epsilon_0 \epsilon^X E + dX$.

in order to calculate the (1) vibration mode and (2) admittance spectrum, respectively.

First, the strain, displacement dynamic modes are obtained from the above constitutive eq. (1). Taking a ∞mm symmetry of a poled piezo-ceramic specimen, the relations between stress, electric field (only E_z exists) and the induced strain in 3-D expression are given by:

$$\begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \end{pmatrix} = \begin{pmatrix} s_{11}^E & s_{12}^E & s_{13}^E & 0 & 0 & 0 \\ s_{12}^E & s_{11}^E & s_{13}^E & 0 & 0 & 0 \\ s_{13}^E & s_{13}^E & s_{33}^E & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44}^E & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{44}^E & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(s_{11}^E - s_{12}^E) \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \\ X_6 \end{pmatrix} + \begin{pmatrix} 0 & 0 & d_{31} \\ 0 & 0 & d_{31} \\ 0 & 0 & d_{33} \\ 0 & d_{15} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ E_3 \end{pmatrix} \quad (33)$$

Note $s_{66}^E = 2(s_{11}^E - s_{12}^E)$ in the ∞mm symmetry like electrically-poled ceramics.

When the plate is very long and thin, X_2 and X_3 may be set equal to zero through the plate. Since shear stress will not be generated by the electric field $E_z (= E_3)$, Eq. (33) is reduced to only one equation:

$$x_1 = s_{11}^E X_1 + d_{31} E_3, \text{ or } X_1 = x_1 / s_{11}^E - (d_{31} / s_{11}^E) E_z. \quad (34)$$

Under AC electric field E_z at an angular frequency ω , we introduce Eq. (34) into Eq. (32). Then, knowing strain definition $x_1 = \partial u / \partial x$ (non-suffix x corresponds to the Cartesian coordinate, u the displacement along the x -axis, and x_1 is the strain along the 1-axis (or x -direction) and $\partial E_z / \partial x = 0$ (due to the equal potential on both top and bottom electrodes), we obtain the following “harmonic vibration equation”:

$$\rho \frac{\partial^2 u}{\partial t^2} = \frac{1}{s_{11}^E} \frac{\partial x_1}{\partial x}, \text{ or } -\omega^2 \rho s_{11}^E u = \frac{\partial^2 u}{\partial x^2}. \quad (35)$$

Supposing the displacement u also vibrates with the frequency of ω , a general solution $u = u_1(x)e^{j\omega t} + u_2(x)e^{-j\omega t}$ is substituted into Eq. (35), and with the boundary condition $X_1 = 0$ at $x = 0$ and L (sample length) (due to the mechanically-free condition at the plate end), the following solutions can be obtained:

$$\begin{aligned} (\text{strain}) \quad x_1 = \partial u / \partial x &= d_{31} E_z [\sin \omega(L-x)/v + \sin(\omega x/v)] / \sin(\omega L)/v \\ &= d_{31} E_z \left(\frac{\cos \left[\frac{\omega(L-2x)}{2v} \right]}{\cos \left(\frac{\omega L}{2v} \right)} \right). \end{aligned} \quad (36)$$

$$(\text{total displacement}) \quad L = u(L) - u(0) = \int_0^L x_1 dx = d_{31} E_z L (2v/\omega L) \tan(\omega L/2v). \quad (37)$$

Here, v is the “sound velocity” in the piezo-ceramic which is expressed by

$$v_{11}^E = \frac{1}{\sqrt{\rho s_{11}^E}}. \quad (38)$$

The strain distribution in Eq. (36) is symmetrically sinusoidal in respect of $x = L/2$ position, and the maximum strain (i.e., nodal line) exists on this line. Note that $\omega \rightarrow 0$ (i.e., pseudo-DC) makes Eq. (36) to $x_1 = d_{31} E_z$; that is, uniform strain distribution on the piezoelectric plate.

Admittance around resonance and antiresonance

When the specimen is utilized as an electrical component such as a filter or a vibrator, the electrical admittance [defined by (induced current)/(applied voltage) ratio] or impedance [(applied voltage)/(induced current)] plays an important role. Now we use the piezoelectric constitutive Eq. (2): $D = \epsilon_0 \epsilon^X E + dX$. The current flow into the specimen is described by the surface charge increment (i.e., “displacement current”), $\partial D_3 / \partial t$. Though the electric field is uniform in the sample due to the surface electrode, the electric displacement D is not uniform because of the stress X distribution due to the mechanical vibration, with the maximum at the nodal line ($x = L/2$). The total displacement current is given by:

$$i = j\omega \int_0^L D_3 dx = j\omega \int_0^L (d_{31} X_1 + \epsilon_0 \epsilon_{33}^X E_z) dx$$

$$= j\omega w \int_0^L [d_{31}\{x_1/s_{11}^E - (d_{31}/s_{11}^E)E_z\} + \epsilon_0\epsilon_{33}^X E_z] dx \quad (39)$$

where w is the plate width. Note that the above current is internal “displacement current” in the piezo-specimen. Thus, the externally measuring current should be $(-i)$. Also $E_z = -\text{grad}(V)$. Using strain distribution in Eq. (36), the admittance for the mechanically free sample is calculated to be:

$$\begin{aligned} Y = \frac{i_{out}}{V} = \frac{-i_{in}}{-E_z \cdot b} &= \frac{j\omega w L}{E_z \cdot b} \int_0^L \left[\left(\frac{d_{31}^2}{s_{11}^E} \right) \left(\frac{\cos\left[\frac{\omega(L-2x)}{2v_{11}^E}\right]}{\cos\left(\frac{\omega L}{2v_{11}^E}\right)} \right) E_z + [\epsilon_0\epsilon_{33}^X - (d_{31}^2/s_{11}^E)] E_z \right] dx \\ &= \frac{j\omega w L}{b} \epsilon_0\epsilon_{33}^{LC} \left[1 + \frac{d_{31}^2}{\epsilon_0\epsilon_{33}^{LC}s_{11}^E} \cdot \frac{\tan(\omega L/2v_{11}^E)}{\omega L/2v_{11}^E} \right] \end{aligned} \quad (40)$$

where the sound velocity of the piezoelectric specimen v_{11}^E is given by Eq. (38), w , L and b are the width, length, and thickness of the rectangular piezo-sample, and V is the applied voltage ($= -E_z \cdot b$).

Here ϵ_{33}^{LC} is the permittivity in a “longitudinally clamped” (LC) specimen, which is given by

$$\epsilon_0\epsilon_{33}^{LC} = \epsilon_0\epsilon_{33}^X - \left(\frac{d_{31}^2}{s_{11}^E} \right) = \epsilon_0\epsilon_{33}^X (1 - k_{31}^2). \quad (k_{31}^2 = d_{31}^2 / \epsilon_0\epsilon_{33}^X s_{11}^E) \quad (41)$$

Note here that this ϵ_{33}^{LC} is different from extensive permittivity ϵ_{33}^X , precisely speaking. ϵ_{33}^{LC} is the permittivity of the specimen mechanically-clamped only along the x (or 1, length) direction, free along z (or 3, polarization direction) or y directions; while ϵ_{33}^X means the permittivity clamped completely in the three directions. The first term $\frac{j\omega w L}{b} \epsilon_0\epsilon_{33}^X$ of admittance Eq. (40) is the “damped capacitance” (longitudinally clamped), and the second term is characterized by $\tan(\omega L/2v)$ which changes from 0, though $+\infty$, to $-\infty$ with ω (neglecting the elastic loss), originated from capacitance change with the mechanical vibration (i.e., “motional capacitance”). Fig. 5 shows an example admittance magnitude and phase spectra for a rectangular piezo-ceramic plate ($L = 20$) around a fundamental longitudinal mode (k_{31}) frequency through the transverse piezoelectric effect (d_{31}) on the basis of Eq. (40). Note that the shown data include losses (Refer to Eq. (46) with losses), and the 3 dB down method to obtain mechanical quality factor Q_m is also inserted in advance.

The piezoelectric resonance is achieved where the admittance becomes infinite or the impedance is zero (neglecting elastic loss). The resonance frequency f_R is calculated from Eq. (40) (by putting $\omega L/2v = 2\pi$ for infinite admittance $\tan(\omega L/2v) = \infty$), and the fundamental frequency is given by

$$f_R = \frac{\omega_R}{2\pi} = \frac{v_{11}^E}{2L} = \frac{1}{2L\sqrt{\rho s_{11}^E}}, \quad (42)$$

which indicates that the resonance frequency of the k_{31} mode corresponds to the primary mechanical resonance directly expressed by a half wavelength on the piezoelectric specimen of length L . On the other hand, the antiresonance state is generated for zero admittance or infinite impedance:

$$\frac{\omega_A L}{2v} \cot\left(\frac{\omega_A L}{2v}\right) = \frac{-d_{31}^2}{\epsilon_{33}^{LC}s_{11}^E} = \frac{-k_{31}^2}{(1 - k_{31}^2)}. \quad (43)$$

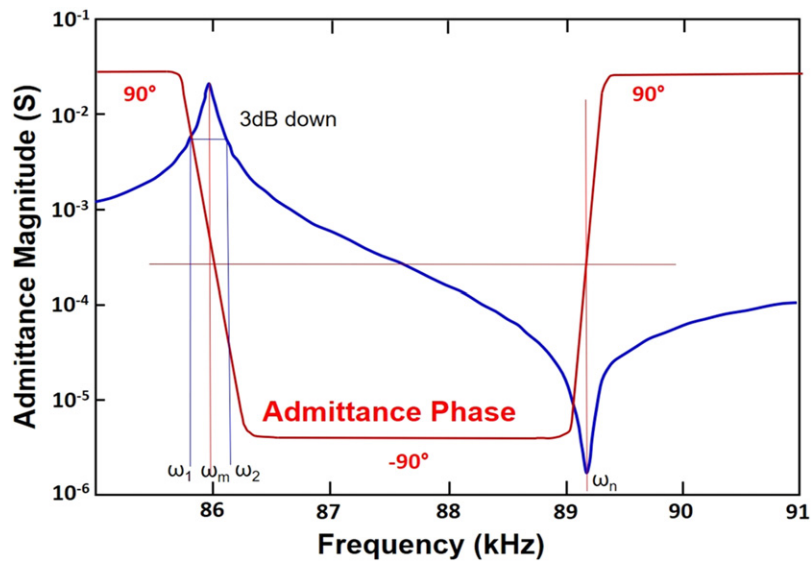


Fig. 5 Admittance spectrum of the k_{31} rectangular plate around its resonance and antiresonance frequencies. ($L = 20$ mm).

which indicates that the antiresonance frequency of the k_{31} mode corresponds to the subsidiary mechanical resonance originated from the electromechanical coupling factor. By the way, the final transformation of Eq. (43) used the definition,

$$k_{31} = d_{31} / \sqrt{s_{11}^E \cdot e_{33}^X}.$$

If we approximate the antiresonance frequency for a small k_{31}^2 (such that $|k_{31}| < 30\%$), we obtain

$$f_A = \frac{\omega_A}{2\pi} = f_R \left(1 + \frac{4}{\pi^2} k_{31}^2 \right), \quad (44)$$

which exhibits the subsidiary resonance correlated with the electromechanical coupling factor clearly, and f_A is slightly higher than f_R (4% for $|k_{31}| = 30\%$). Though we will not discuss on the k_{33} mode, the situation is rather different (opposite) from the above k_{31} case. Refer to Ref (Uchino, 2020b). for further discussion.

Now we expand the resonance/antiresonance dynamic equations by integrating dielectric, elastic and piezoelectric losses. We introduce the “complex parameters” into the admittance formula Eq. (40) (Uchino, 2020b):

$$\begin{cases} e_{33}^{X*} = e_{33}^X (1 - j \tan \delta'_{33}) \\ s_{11}^{E*} = s_{11}^E (1 - j \tan \phi'_{11}) \\ d_{31}^* = d_{31} (1 - j \tan \theta'_{31}) \end{cases} \quad (45)$$

where $\tan \delta'_{33}$, $\tan \phi'_{11}$ and $\tan \theta'_{31}$ are “intensive” dielectric, elastic and piezoelectric loss factors.

$$Y = Y_d + Y_m$$

$$= j\omega C_d (1 - j \tan \delta''_{33}) + j\omega C_d K_{31}^2 \left[1 - j (2 \tan \theta'_{31} - \tan \phi'_{11}) \right] \left[\tan(\omega L / 2\nu_{11}^{E*}) / (\omega L / 2\nu_{11}^{E*}) \right], \quad (46)$$

where the following notations are adopted:

$$C_0 = (\omega L / b) \epsilon_0 \epsilon_{33}^X \text{ (free electrostatic capacitance, real number)} \quad (47)$$

$$C_d = (1 - k_{31}^2) C_0 \text{ (damped/clamped capacitance, real number)} \quad (48)$$

$$K_{31}^2 = \frac{k_{31}^2}{1 - k_{31}^2} \quad (49)$$

Note that the loss for the first term (“damped/clamped” admittance) is represented by the dielectric loss $\tan \delta''$:

$$\tan \delta''_{33} = [1 / (1 - k_{31}^2)] \left[\tan \delta'_{33} + k_{31}^2 (\tan \phi'_{11} - 2 \tan \theta'_{31}) \right] \quad (50)$$

Though the formula $\tan \delta''_{33}$ is similar to the “extensive” non-prime loss $\tan \delta$ (Eq. (28)), because the extensive loss should be under 3D clamped condition, not under just 1D (thickness direction) longitudinally clamped as in the k_{31} case. Taking into account

$$\nu_{11}^{E*} = \frac{1}{\sqrt{\rho s_{11}^E (1 - j \tan \phi'_{11})}} = \nu_{11}^E \left(1 + j \frac{\tan \phi'_{11}}{2} \right), \quad (51)$$

we further calculate $1 / \tan(\frac{\omega L}{2\nu})$ with an expansion-series approximation around the A-type resonance frequency $\omega_A L / 2\nu = 2\pi$. [“A-type” and “B-type” resonances are alternatively used for the “resonance” and “antiresonance” conventionally when we treat these two modes equally.] Under the consideration that the resonance state is defined in this case for the minimum impedance point, and using new frequency parameters,

$$\Omega_A = \frac{\omega_A L}{2\nu_{11}^E} = \frac{\pi}{2}, \quad \Delta\Omega_A = \Omega - \frac{\pi}{2} (\ll 1), \quad (52)$$

with the relationship around the A-type resonance frequency.

$$\frac{1}{\tan \Omega} = \cot \left(\frac{\pi}{2} + \Delta\Omega_A - j \frac{\pi}{4} \tan \phi'_{11} \right) = \Delta\Omega_A - j \frac{\pi}{4} \tan \phi'_{11},$$

the motional admittance Y_m (by neglecting Y_d because of the magnitude difference) is approximated around the first resonance frequency ω_A by

$$Y_m = j \frac{8}{\pi^2} \omega_A C_d K_{31}^2 \left[1 - j (2 \tan \theta'_{31} - \tan \phi'_{11}) \right] / \left[\left(\frac{4}{\pi} \right) \Delta\Omega_A - j \tan \phi'_{11} \right]. \quad (53)$$

The maximum Y_m is obtained at $\Delta\Omega_A = 0$:

$$Y_m^{\max} = \frac{8}{\pi^2} \omega_A C_0 K_{31}^2 \frac{1}{\tan \phi'_{11}} = \frac{8}{\pi^2} \omega_A C_0 K_{31}^2 Q_A, \quad (54)$$

The mechanical quality factor for the A-type resonance $Q_A = (\tan \phi'_{11})^{-1}$ can be proved as follows: Q_A is defined by $Q_A = \omega_A / 2\Delta\omega$, where $2\Delta\omega$ is a full width of the 3 dB down (i.e., $1/\sqrt{2}$, because $20 \log_{10}(1/\sqrt{2}) = -3.01$) of the maximum value $Y_m^{\max}$ at $\omega = \omega_A$. Refer to Fig. 5. Since $Y = Y_m^{\max} / \sqrt{2}$ can be obtained when the “conductance = susceptance”; $\Delta\Omega_A = (\pi/4) \tan \phi'_{11}$

[see the denominator of Eq. (53)],

$$Q_A = \frac{\Omega_A}{2\Delta\Omega_A} = (\pi/2)/2(\pi/4)\tan\phi'_{11} = [\tan\phi'_{11}]^{-1} \quad (55)$$

Similarly, the maximum displacement u^{max} is obtained at $\Delta\Omega = 0$:

$$u^{max} = \frac{8}{\pi^2} d_{31} E_z L Q_A. \quad (56)$$

The maximum displacement at the resonance frequency is $(8/\pi^2)Q_A$ times larger than that at a non-resonance frequency, $d_{31}E_zL$. Under the constant voltage/field drive, the admittance and displacement are amplified at the resonance frequency; while under the constant current drive, the displacement u and the impedance Z are amplified at the antiresonance frequency by the factor of $(8/\pi^2)Q_B$, as explained below.

On the other hand, a higher quality factor at the antiresonance is usually observed in comparison with that at the resonance point (Hirose *et al.*, 1996; Mezheritsky, 2002) in most of the Pb-based piezo-ceramics, the phenomenological reason of which was interpreted by Mezheritsky from the combination of three loss factors (Mezheritsky, 2002). In this manuscript, we introduce our user-friendly formula to determine piezoelectric losses by analyzing the admittance/impedance spectra at resonance and antiresonance (Uchino and Hirose, 2001; Uchino *et al.*, 2011a). The antiresonance corresponds to the minimum admittance of Eq. (40):

$$Y = j \frac{\omega L}{b} \epsilon_0 \epsilon_{33}^X \left[(1 - k^2) + k^2 \frac{\tan(\omega L/2v_{11}^E)}{(\omega L/2v_{11}^E)} \right] = j\omega C_0 \left[(1 - k_{31}^2) + k_{31}^2 \frac{\tan(\Omega_{11})}{\Omega_{11}} \right]$$

Here, $v_{11}^E = 1/\sqrt{\rho s_{11}^E}$, $\Omega_{11} = \omega L/2v_{11}^E$, and $k_{31}^2 = \frac{d_{31}^2}{\epsilon_0 \epsilon_{33}^X s_{11}^E}$.

In the resonance discussion, we neglected the damped admittance, because the motional admittance is significantly large due to $\tan(\omega L/2v_{11}^E) \nearrow \infty$. On the contrary, in the antiresonance discussion, we consider basically the subtraction between the damped and motional admittances (due to 180° phase difference); that is, the total admittance should be exactly to zero when the loss is not included, or is only the minimum when we consider the losses (that is, complex parameters) in Eq. (46).

We introduce the normalized admittance ($Y' = Y/j\omega C_0$) for calculation simplicity:

$$Y' = 1 - k_{31}^2 + k_{31}^2 \frac{\tan(\Omega_{11})}{\Omega_{11}}. \quad \left[\Omega_{11} = \frac{\omega L}{2v_{11}^E} \right] \quad (57)$$

Since the expansion series of $\tan\Omega$ is convergent in this case, taking into account Eq. (45) and other loss factors, Eq. (57) leads to

$$Y' = 1 - k_{31}^2 \left[1 - j(2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11}) \right] + k_{31}^2 \left[1 - j(2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11}) \right] \frac{\tan\Omega_{11}^*}{\Omega_{11}^*}. \quad (58)$$

Note that the “electromechanical coupling k_{31}^2 loss” $(2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11})$ contributes significantly in this antiresonance discussion. Recall the remark in the last part of Section “Electromechanical Coupling Factor” We separate Y' into conductance G (real part) and susceptance B (imaginary part) as $Y' = G + jB$:

$$G = 1 - k_{31}^2 + k_{31}^2 \frac{\tan\Omega}{\Omega}. \quad (59)$$

$$B = \left(k_{31}^2 - k_{31}^2 \frac{\tan\Omega}{\Omega} \right) (2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11}) - \frac{k_{31}^2}{2} \left(\frac{1}{\cos^2\Omega} - \frac{\tan\Omega}{\Omega} \right) \tan\phi'_{11}. \quad (60)$$

The antiresonance frequency Ω_B should satisfy “ $G = 0$ ”, or $1 - k_{31}^2 + k_{31}^2 \frac{\tan\Omega_B}{\Omega_B} = 0$. Using new parameters,

$$\Omega = \Omega_B + \Delta\Omega_B, \quad (61)$$

$\Delta\Omega_B$ is also a small number, and the first order approximation can be utilized. Neglecting high order term which has two or more small factors (loss factor or $\Delta\Omega_B$), we further approximate Eqs. (59) and (60). Since the antiresonance quality factor Q_B is given by

$$Q_{B,31} = \frac{\Omega_B}{2|\Delta\Omega_B|}, \quad (62)$$

where the above $\Delta\Omega_B$ should satisfy the 3 dB-up admittance point; that is, “ $G = B$ ”. We can obtain the final formulas for both A-type and B-type mechanical quality factors:

$$\left\{ \frac{1}{Q_{B,31}} = \frac{1}{Q_{A,31}} - \frac{2}{1 + \left(\frac{1}{k_{31}} - k_{31} \right)^2 \Omega_B^2} \left(2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11} \right) \right\} \quad (63)$$

You may understand that k_{31} mode, where the wave propagation direction with the electrode is perpendicular to the spontaneous polarization direction, the primary mechanical resonance (a half wavelength vibration of the plate length) corresponds to the “resonance mode” with the sound velocity s_{11}^E , and the “antiresonance mode” corresponds to the subsidiary mode via the

electromechanical coupling. Also from the Eq. (63), we can understand that when $(2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11}) > 0$, $Q_{B,31} > Q_{A,31}$; while $(2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11}) < 0$, $Q_{B,31} < Q_{A,31}$.

Recall the experimental admittance spectrum of the k_{31} rectangular plate ($L = 20$ mm) around its resonance and antiresonance frequencies in Fig. 5. In the Pb-based perovskite piezoelectric ceramics such as PZTs, $Q_{B,31} > Q_{A,31}$ is usually observed; that is, $\tan\theta'_{31} > (\frac{1}{2})(\tan\delta'_{33} + \tan\phi'_{11})$ in PZTs. The intensive “piezoelectric loss” seems to be larger than the “average of dielectric and elastic losses”.

Eq. (63) indicates how to separately measure the three losses in experiments, which are described in Section “High Power Piezoelectric Characterization System (HiPoCS)”. Mechanical quality factors Q_A (resonance) and Q_B (antiresonance) for other modes such as k_{33} , k_t , k_p and k_{15} have been calculated and summarized in Section “Loss and Mechanical Quality Factor in Other Modes” (Uchino *et al.*, 2011a; Zhuang *et al.*, 2009a, 2010).

Resonance and antiresonance vibration modes

The resonance (A-type) and antiresonance (B-type) states are both mechanical resonance states with amplified strain/displacement states, but they are very different from the electrical driving viewpoints. The mode difference is described by the following intuitive model. Let us start from the case of a high electromechanical coupling material with k almost equal to 1, the resonance or antiresonance states appear for $\tan(\omega L/2v) = \infty$ or 0 [i.e., $\omega L/2v = (m-1/2)\pi$ or $m\pi$ (m : integer)], respectively. Based on the fundamental resonance frequency $f_A (= v_{11}^E/2L)$, the second and third resonance frequencies are represented as $3f_A$ and $5f_A$; the antiresonance frequencies should be $2f_A$, $4f_A$ and $6f_A$, successively. The strain amplitude x_1 distribution for each state [calculated using Eq. (36)] is illustrated in Fig. 6. In the resonance state, the strain distribution is basically sinusoidal with the maximum at the center of plate ($x = L/2$) (see the numerator). When ω is close to ω_A , $(\omega_A L/2v) = \pi/2$, leading to the denominator $\cos(\omega_A L/2v) \rightarrow 0$. Significant strain amplification ($\propto Q_m$) is obtained. It is worth noting that the stress X_1 is zero at the plate ends ($x = 0$ and L), but the strain x_1 is not precisely zero, but is equal to $d_{31}E_z$. According to this large strain amplitudes, large capacitance changes (called “motional capacitance”) are induced, and under a constant applied voltage the current can easily flow into the device (i.e., admittance Y is infinite). To the contrary, at the antiresonance (B-type), the strain induced in the specimen compensates completely (because extension and compression are compensated in one wave on the specimen length), resulting in no motional capacitance change, and the current cannot flow easily into the sample (i.e., admittance Y zero). Thus, for a high k_{31} material the first antiresonance frequency f_B should be almost twice as large as the first resonance frequency f_A .

It is notable that both resonance and antiresonance states are in the mechanical resonance, which can create large strain in the sample under minimum input electrical energy. When we use a constant voltage supply, the specimen vibration is excited only at the resonance mode, because the electrical power is very small at the antiresonance mode. This provides a common misconception to junior engineers that “the antiresonance is not a mechanical resonance”. In contrast, when we use a constant current supply, the vibration is excited only at the antiresonance, instead. The stress X_1 at the plate ends ($x = 0$ and L) is supposed to be zero in both cases. However, though the strain x_1 at the plate ends is zero/very small (precisely, $d_{31}E_z$, because of low voltage and high current drive) for the resonance, the strain x_1 is large (actually the maximum) for the antiresonance (because of high voltage and low current drive). This means that there is only one vibration node (i.e., zero displacement point) at the plate center for the resonance (Top-left in Fig. 6), and there are additional two nodes at both plate ends for the first antiresonance (Top-right in Fig. 6). The reason is from the antiresonance drive, i.e., high voltage/low current (minimum power) drive due to the high impedance. The converse piezo-effect strain under E directly via d_{31} (uniform strain in the sample) superposes on the mechanical resonance strain distribution (distributed strain with nodes in the sample). Thus, two strains of which have exactly the same level theoretically at the antiresonance for $k_{31} \approx 1$.

In a typical case, where $k_{31} = -0.3$ [sometimes “-” is omitted just to discuss the magnitude], because the damped capacitance $C_d = (1 - k_{31}^2)C_0$ is large, the antiresonance state varies from the previously-mentioned mode and becomes closer to the resonance mode (Top-center in Fig. 6). The low-coupling material exhibits an antiresonance mode where the capacitance change due to the size change (“motional capacitance”) is compensated completely by the current required to charge up the static capacitance (called “damped capacitance”). Thus, the antiresonance frequency f_B will approach the resonance frequency f_A with a similar vibration mode [$f_B = f_A(1 + \frac{4}{\pi^2}k_{31}^2)$ indicates only 3.6% shift from f_A], and the vibration mode seems to be close to the resonance configuration with the antinode position slightly inside the rectangular plate edges. This is the background reason why the author’s group proposes the “vibration velocity constant” measuring method for measuring the resonance and antiresonance

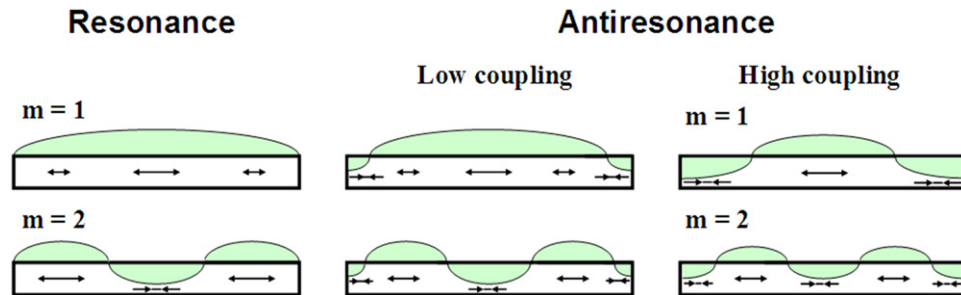


Fig. 6 Strain distribution in the resonant and antiresonant states for the k_{31} type piezoelectric plate.

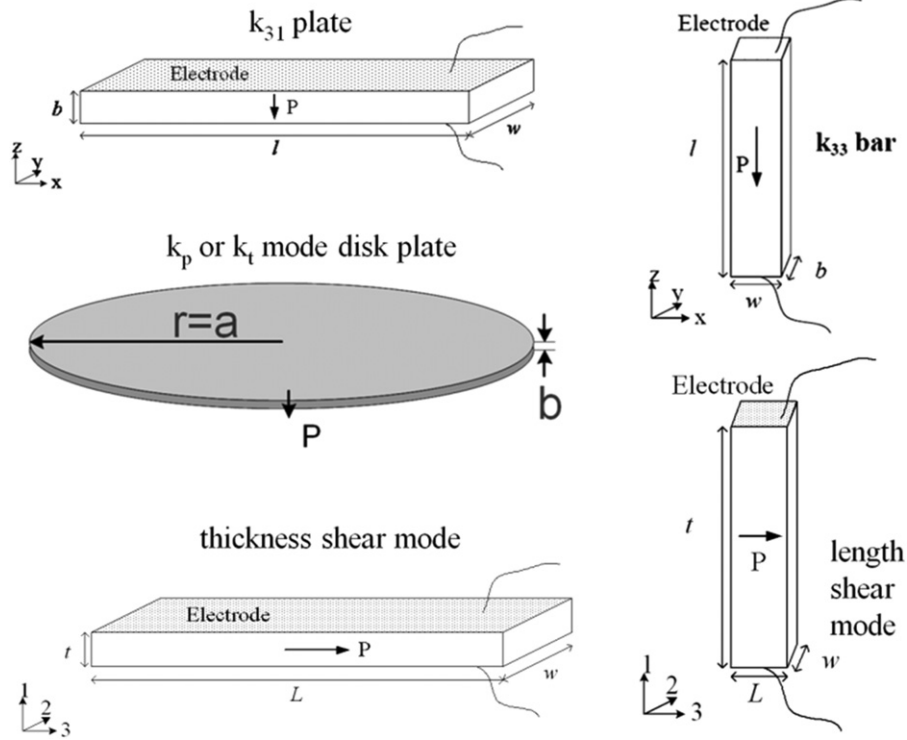


Fig. 7 Sketches of the sample geometries for five required vibration modes.

spectrum precisely even under high-power level, as discussed in Section “High Power Piezoelectric Characterization System (HiPoCS)”.

It is notable that the mechanical resonance of a k_{31} -type rectangular plate can also be excited under cyclic stress application along the x -axis. In this case, by sweeping the stress frequency, only one mechanical resonance is observed; $f_A (= \nu_{11}^E/2L)$ when the rectangular plate specimen is short-circuited, while $f_B = f_A(1 + \frac{4}{\pi^2}k_{31}^2)$ (for a small k_{31} material) when the specimen is open-circuited between the top and bottom electrodes. The electrical boundary condition changes significantly the elastic compliance in the piezoelectric materials. This is the background reason of the burst mode measuring method of the resonance and anti-resonance mechanical quality factors in Section “High Power Piezoelectric Characterization System (HiPoCS)”.

Loss and mechanical quality factor in other modes

To obtain the loss factor matrix, five vibration modes need to be characterized in PZT's, as shown in Fig. 7. The methodology is based on the equations of quality factors Q_A (resonance) and Q_B (antiresonance) in various modes with regard to loss factors and other properties (Zhuang *et al.*, 2009a, 2010). We measure Q_A and Q_B for each mode by using the 3 dB-up/down method in the impedance/admittance spectra (See Fig. 7). In addition to some derivations based on fundamental relations of the material properties, all the 20 loss factors can be / . obtained for piezoelectric ceramics. We derived the relationships between mechanical quality factors Q_A (resonance) and Q_B (antiresonance) in all required five modes. The results are summarized below:

(a) k_{31} mode:

$$Q_{A,31} = \frac{1}{\tan\phi'_{11}}$$

$$\frac{1}{Q_{B,31}} = \frac{1}{Q_{A,31}} + \frac{2}{1 + \left(\frac{1}{k_{31}} - k_{31}\right)^2 \Omega_{B,31}^2} \left(\tan\delta'_{33} + \tan\phi'_{11} - 2\tan\theta'_{31} \right)$$

$[\tan\delta'_{33}, \tan\phi'_{11}, \tan\theta'_{31}]$: intensive loss factors for $\epsilon_{33}^T, s_{11}^E, d_{31}$; $\Omega_{B,31}$: antiresonance frequency]

$$\Omega_{A,31} = \frac{\omega_p L}{2\nu_{11}^E} = \frac{\pi}{2} \left[\nu_{11}^E = 1/\sqrt{\rho s_{11}^E} \right]; \Omega_{B,31} = \frac{\omega_p L}{2\nu_{11}^E} \left[1 - k_{31}^2 + k_{31}^2 \frac{\tan\Omega_B}{\Omega_B} = 0 \right]$$

(b) k_t mode:

$$Q_{B,t} = \frac{1}{\tan\phi_{33}}$$

$$\frac{1}{Q_{A,t}} = \frac{1}{Q_{B,t}} + \frac{2}{k_t^2 - 1 + \Omega_A^2/k_t^2} (\tan\delta_{33} + \tan\phi_{33} - 2\tan\theta_{33})$$

$$\Omega_{B,t} = \frac{\omega_b L}{2v_{33}^D} = \frac{\pi}{2} \left[v_{33}^D = 1/\sqrt{\rho/c_{33}^D} \right]; \Omega_{A,t} = \frac{\omega_a L}{2v_{33}^D} \quad [\Omega_{A,t} = k_t^2 \tan\Omega_{A,t}].$$

(c) k_{33} mode:

$$Q_{B,33} = \frac{1 - k_{33}^2}{\tan\phi'_{33} - k_{33}^2(2\tan\theta'_{33} - \tan\delta'_{33})} \left[\approx \frac{1}{\tan\phi'_{33}} \right]$$

$$\frac{1}{Q_{A,33}} = \frac{1}{Q_{B,33}} + \frac{2}{k_{33}^2 - 1 + \frac{\Omega_{A,33}^2}{k_{33}^2}} (2\tan\theta'_{33} - \tan\delta'_{33} - \tan\phi'_{33})$$

$$\left[\approx \frac{1}{Q_{B,33}} + \frac{2}{k_{33}^2 - 1 + \Omega_{A,33}^2/k_{33}^2} (\tan\delta_{33} + \tan\phi_{33} - 2\tan\theta_{33}) \right]$$

$$\Omega_{B,33} = \frac{\omega_b L}{2v_{33}^D} = \frac{\pi}{2} \left[v_{33}^D = 1/\sqrt{\rho s_{33}^D} \right]; \Omega_{A,33} = \frac{\omega_a L}{2v_{33}^D} \quad [\Omega_{A,33} = k_{33}^2 \tan\Omega_{A,33}]$$

(d) k_{15} mode (constant E – length shear mode):

$$Q_{A,15}^E = \frac{1}{\tan\phi'_{55}}$$

$$\frac{1}{Q_{B,15}^E} = \frac{1}{Q_{A,15}^E} - \frac{2}{1 + \left(\frac{1}{k_{15}} - k_{15}\right)^2 \Omega_B^2} (2\tan\theta'_{15} - \tan\delta'_{11} - \tan\phi'_{55})$$

$$\Omega_{A,15} = \frac{\omega_a L}{2v_{55}^E} = \frac{\omega_a L}{2} \sqrt{\rho s_{55}^E}; \Omega_{B,15} = \frac{\omega_b L}{2v_{55}^E} \quad \left[1 - k_{15}^2 + k_{15}^2 \frac{\tan\Omega_B}{\Omega_B} = 0 \right]$$

(e) k_{15} mode (constant D – thickness shear mode):

$$Q_{B,15}^D = \frac{1}{\tan\phi_{55}}$$

$$\frac{1}{Q_{A,15}^D} = \frac{1}{Q_{B,15}^D} + \frac{2}{k_{15}^2 - 1 + \Omega_{A,15}^2/k_{15}^2} (\tan\delta_{11} + \tan\phi_{55} - 2\tan\theta_{15})$$

$$\Omega_{B,15} = \frac{\omega_b t}{2v_{55}^D} = \frac{\omega_b t}{2} \sqrt{\frac{\rho}{c_{55}^D}}; \Omega_{A,15} = \frac{\omega_a L}{2v_{55}^D} \quad [\Omega_A = k_{15}^2 \tan\Omega_A]$$

Note that because k_{31} and k_{33}/k_t modes possess E-constant and D-constant constraints, respectively, in k_{31} , the resonance frequency is directly related with v_{11}^E or s_{11}^E as $f_A = \frac{v_{11}^E}{2L} = 1/2L\sqrt{\rho s_{11}^E}$; while in k_{33}/k_t , the antiresonance frequency is directly related with v_{33}^D or s_{33}^D , c_{33}^D as $f_B = \frac{v_{33}^D}{2L} = 1/2L\sqrt{\rho s_{33}^D}$ or $1/2b\sqrt{\rho/c_{33}^D}$. It is important to distinguish k_{33} ($X_1 = X_2 = 0, x_1 = x_2 \neq 0$) from k_t ($X_1 = X_2 \neq 0, x_1 = x_2 = 0$) from the boundary conditions. The argument is valid only when the length of a rod k_{33} is not very long ($c_{33}^D \approx 1/s_{33}^D$). The antiresonance in k_{31} and the resonance in k_{33}/k_t are subsidiary, originated from the electromechanical coupling factors. We can also derive the relation for the electromechanical coupling factor losses from Eq. (20):

$$(2\tan\theta' - \tan\delta' - \tan\phi') = -(2\tan\theta - \tan\delta - \tan\phi). \quad (64)$$

Because the side is not clamped ($x_1 = x_2 \neq 0$) in the k_{33} mode, 1-D Eq. (64) is not completely true. Thus, “ $\approx$ ” is used in the above for roughly translating the intensive losses into the extensive losses. To the contrary, because the side is clamped ($x_1 = x_2 = 0$) in the k_t mode, 1-D Eq. (64) is precisely true.

It is important to discuss the assumption in the IEEE Standard: $Q_A = Q_B$. This situation occurs only when $(2\tan\theta' - \tan\delta' - \tan\phi') = 0$, or $\tan\theta' = (\frac{1}{2})(\tan\delta' + \tan\phi')$. The IEEE Standard discusses only when the piezoelectric loss is equal to the average value of the dielectric and elastic losses, which exhibits a serious contradiction to the PZT experimental results $Q_A < Q_B$, as introduced in Fig. 5.

It is worth noting that the intensive piezoelectric loss is larger than the average of the dielectric and elastic intensive losses in Pb-contained piezo-ceramics. We introduce in Section “High-Power Piezoelectric Materials” that in Pb-free piezoelectric ceramics, the piezoelectric loss contribution is not significant, and $\frac{1}{2}(\tan\delta'_{33} - \tan\phi'_{11}) > \tan\theta'_{31}$, which may suggest different loss mechanisms in different piezo-ceramics.

Heat Generation in Piezoelectrics

We introduce the heat generation in PZT-based actuators studied under a large electric field applied (1 kV/mm or higher) at an off-resonance frequency and under a relatively small electric field applied (100 V/mm) at a resonance frequency. The reader learns how the heat generation is originated from the three losses in piezoelectrics.

Heat Generation at off-Resonance

Zheng *et al.* (1996) reported the heat generation at an off-resonance frequency from various sizes of multilayer (ML) type piezoelectric ceramic (soft PZT) actuators. The temperature change with time in the actuators was monitored when driven at 3 kV/mm (high electric field) and 300 Hz (low frequency). Fig. 8(a), and (b) plot time dependence of the temperature rise and the saturated temperature as a function of V_e/A , respectively. Here V_e is the effective volume (electrode overlapped part) and A is the surface area. Suppose that the temperature was uniformly generated in a bulk sample (no significant stress distribution), this linear relation is reasonable because the volume V_e generates the heat evenly and this heat is dissipated through the surface area A . Thus, if we need to suppress the temperature rise, a small V_e/A design is preferred.

According to the law of energy conservation, the amount of heat stored in the piezoelectric, which is just the difference between the rate at which heat is generated, q_g , and that at which the heat is dissipated, q_d , can be expressed as

$$q_g - q_d = V\rho C_p \frac{dT}{dt}, \quad (65)$$

where it is assumed a uniform temperature distribution existing throughout the specimen and V is the total volume, ρ is the mass density, and C_p is the “specific heat” of the specimen. The heat generation in the piezoelectric is attributed to losses. Thus, the rate of heat generation, q_g , can be expressed as:

$$q_g = wfV_e, \quad (66)$$

where w is the loss per driving cycle per unit volume, f is the driving frequency, and V_e is the effective volume of active ceramic (no-electrode parts are omitted). According to the measuring conditions (off-resonance, no significant stress in the sample), this w corresponds primarily to the “dielectric hysteresis loss” (i.e., P - E hysteresis), w_e , which is expressed in Eq. (6b) in terms of the “intensive dielectric loss” $\tan\delta$ as: $w = w_e = \pi\epsilon^X\epsilon_0 E_0^2 \tan\delta$.

If we neglect the transfer of heat through conduction (electric lead is very thin), the rate of heat dissipation (q_d) from the specimen is the sum of the rates of heat flow by radiation (q_r) and by convection (q_c):

$$q_d = q_r + q_c = eA\sigma(T^4 - T_0^4) + h_c A(T - T_0), \quad (67)$$

where e is the emissivity of the sample, A is the sample surface area, σ is the Stefan-Boltzmann constant, T_0 is the initial sample temperature, h_c is the average “convective heat transfer coefficient”. Thus, Eq. (65) can be written in the form:

$$wfV_e - Ak(T)(T - T_0) = V\rho C_p \frac{dT}{dt}, \quad (68)$$

where the quantity

$$k(T) = \sigma e(T^2 + T_0^2)(T + T_0) + h_c \quad (69)$$

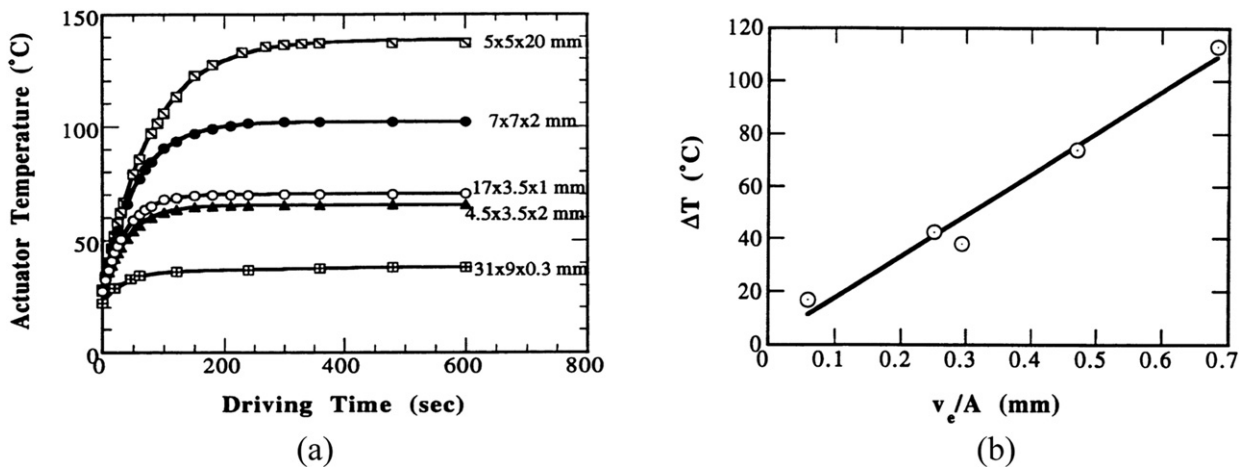


Fig. 8 (a) Device temperature change with driving time for ML actuators of various sizes. (b) Temperature rise at off-resonance versus V_e/A in various size soft PZT ML actuators, where V_e and A are the effective volume and the surface area, respectively.

is the overall “heat transfer coefficient”. If we assume that $k(T)$ is relatively insensitive to temperature change (if the temperature rise is not large), solving Eq. (68) for the rise in temperature of the piezoelectric sample yields:

$$T - T_0 = \frac{wfV_e}{k(T)A} (1 - e^{-t/\tau}), \quad (70)$$

where the time constant τ is expressed as:

$$\tau = \frac{\rho C_p V}{k(T)A}. \quad (71)$$

As $t \rightarrow \infty$, the maximum temperature rise in the sample becomes:

$$\Delta T = \frac{wfV_e}{k(T)A}, \quad (72)$$

while, as $t \rightarrow 0$, the initial rate of temperature rise is given by

$$\frac{dT}{dt} = \frac{w_T f V_e}{\rho C_p V} = \frac{\Delta T}{\tau}, \quad (73)$$

where w_T can be regarded under these conditions as a measure of the total loss of the piezoelectric. The dependences of $k(T)$ on applied electric field and frequency are shown in Fig. 9(a) and (b), respectively. Note that $k(T)$ is relatively constant, as long as the driving voltage or frequency is not very high ($E < 1$ kV/mm, $f < 0.3$ kHz). The total loss, w_T , as calculated from Eq. (73) is given for three multilayer specimens in Table 1. The experimentally determined “ $P - E$ hysteresis losses” measured under stress-free conditions (Eq. (6b)) are also listed in the table for comparison. It can be seen that the extrinsic $P - E$ hysteresis loss agrees well ($\sim 90\%$) with the calculated total loss associated with the heat generated in the driven piezoelectrics (Uchino *et al.*, 1998).

Heat Generation Under Resonance Conditions

Heat diffusion equation

Tashiro *et al.* (1997) observed the heat generation in a rectangular piezoelectric plate during a resonating drive. Even though the electric field is not large, considerable heat is generated due to the induced large strain/ stress under the resonance. The maximum heat generation was observed in the nodal regions for the resonance vibration, which correspond to the locations where the maximum strains/stresses are generated. The author’s group also worked on the heat generation numerically in rectangular piezoelectric k_{31} plates when driven at the resonance (Uchino *et al.*, 1989). Fig. 10 shows the temperature distribution profile in a PZT plate specimen observed by a pyroelectric infrared camera, in which the temperature profiles are shown in the specimen driven at the first (28.9 kHz) (a) and second resonance (89.7 kHz) (b) modes. The highest temperature (emphasized by arrows) is evident at the nodal areas of the specimen. This observation supports that the heat generation in a resonating sample is governed by the intensive elastic loss, $\tan\phi''$.

As we discussed in Section “Admittance around resonance and antiresonance”, the resonance and antiresonance are both mechanical resonances with the impedance equal to zero, and Q_B at antiresonance is higher than Q_A at resonance in PZT’s, which

indicates the better efficiency at the antiresonance drive than at the resonance. Fig. 11(a) and (b) demonstrate temperature variations in a PZT plate specimen driven at the antiresonance (a) and resonance frequency (b) under the same “vibration velocity” (i.e., the same output mechanical energy), which clearly exhibit lower temperature rise in the antiresonance. Numerical profiles of the temperature distribution for the A- and B-type resonance modes are shown in Fig. 11(c), which seems to be sinusoidal curves to be used for the model simulation below.

Extending the heat flow equation Eq. (65) for a uniform temperature profile, we need to define the coordinate-dependent energy generation profile at the resonance mode (Shekhani and Uchino, 2014a). An 1-D heat transfer model for the k_{31} mode

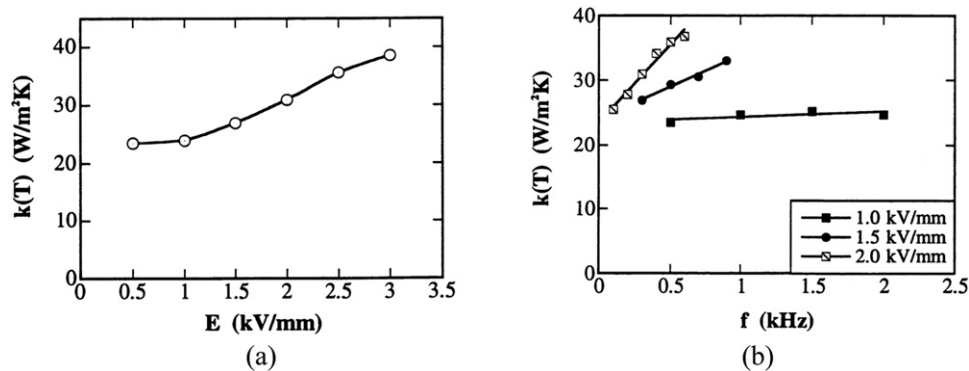
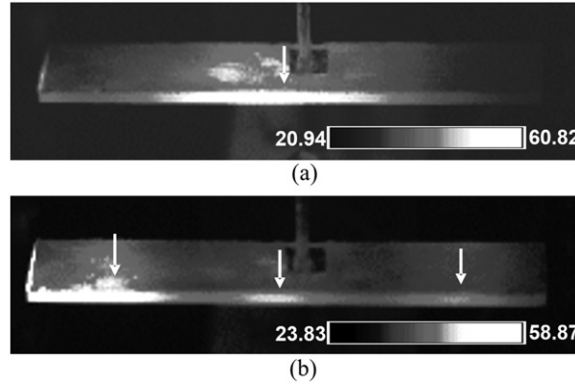


Fig. 9 Overall heat transfer coefficient, $k(T)$, plotted as a function of applied electric field (a), and of frequency (b) for a PZT ML actuator with dimensions of $7 \times 7 \times 2$ mm³ driven at 400 Hz.

Table 1 Loss and overall heat transfer coefficient for PZT multilayer samples driven under $E = 3 \text{ kV/mm}$, $f = 300 \text{ Hz}$

Actuator	$4.5 \times 3.5 \times 2.0 \text{ mm}^3$	$7.0 \times 7.0 \times 2.0 \text{ mm}^3$	$17 \times 3.5 \times 1.0 \text{ mm}^3$
$w_T (\text{kJ/m}^3) \left[= \frac{\rho c_p V}{N_e} \left(\frac{dT}{dt} \right)_{t \rightarrow 0} \right]$	19.2	19.9	19.7
P - E hysteresis loss (kJ/m^3)	18.5	17.8	17.4
$k(T) (\text{W/m}^2 \text{ K})$	38.4	39.2	34.1

Note: Reproduced from Zheng, J., Takahashi, S., Yoshikawa, S., Uchino, K., de Vries, J.W.C., 1996. Heat generation in multilayer piezoelectric actuators. J. Am. Ceram. Soc. 79, 3193–3198.

**Fig. 10** Temperature distribution in a PZT k_{37} plate specimen observed by a pyroelectric infrared camera. Driven at (a) the first resonance and (b) the second resonance mode.

piezoelectric rectangular plate was developed. In comparison with the off-resonance model, where the heat is generated primarily from the dielectric loss and the uniform temperature distribution profile due to no particular stress in the specimen, the resonance case generates the heat originated from the elastic loss on a sinusoidal stress distribution in a specimen. Because of the initial heat source is sinusoidally distributed in the specimen, we need to integrate the “thermal diffusivity” of the piezo-ceramic in order to analyze the temperature distribution of the sample.

We set the following assumptions for developing the heat diffusion equation:

- (1) 1-D heat conduction in the specimen.
- (2) Heat generation is proportional to strain squared (i.e., elastic energy), distributed on the specimen.
- (3) Heat dissipation via convection (to air) and radiation, similar to Section “Heat Generation at off-Resonance”.

Using a temperature parameter $T(x, t)$, which is defined as temperature of a sliced volume Δx from the position coordinate x to $(x + \Delta x)$ at time t , the following equation is assumed:

$$\frac{\partial T(x, t)}{\partial t} = \frac{\kappa}{c_p \rho} \frac{\partial^2 T(x, t)}{\partial x^2} + \frac{q_g(x)}{c_p \rho} - \frac{h_d P}{c_p \rho A} [T(x, t) - T_{air}] \quad (74)$$

where κ is “thermal conductivity” (unit: W/m K), c_p is specific heat (unit: J/kg K), and a new parameter $\frac{\kappa}{c_p \rho} = \alpha$ is called “thermal diffusivity” (unit: m^2/s). The first term of the right-hand-side of Eq. (74) describes the temperature distribution in respect of the position x , which changes the shape with time. The second term corresponds to the temperature increment caused by heat generation per mass (divided by $c_p \rho$). Third term indicates the heat dissipation proportional to the temperature difference ΔT from the ambient temperature.

Regarding the heat generation, we further assume that q_g is expressed in proportion to the square of the strain:

$$q_g(x) = g_h \cos^2 \left(\frac{\pi x}{L} \right) \quad (75)$$

The heat dissipation h_d can be approximated in proportion to $[T - T_{air}]$, similar to “heat transfer coefficient” introduced in Eq. (69).

Temperature distribution profile change with time

We prepared a piezoelectric k_{31} rectangular plate specimen with $80 \times 14 \times 2 \text{ mm}^3$ in size with a hard PZT composition (APC 841, American Piezo Company, USA) for both admittance and thermal imaging observation purposes. We used a “constant vibration velocity method” for the measurements under 300 mm/s rms . Fig. 12(a) shows the temperature distribution profile change with time after driving. You can notice that the plate edge temperature increases rather significantly with time lapse, primarily due to the “thermal diffusion” in the PZT from the nodal highest point to the edge lowest temperature point. The saturated temperature

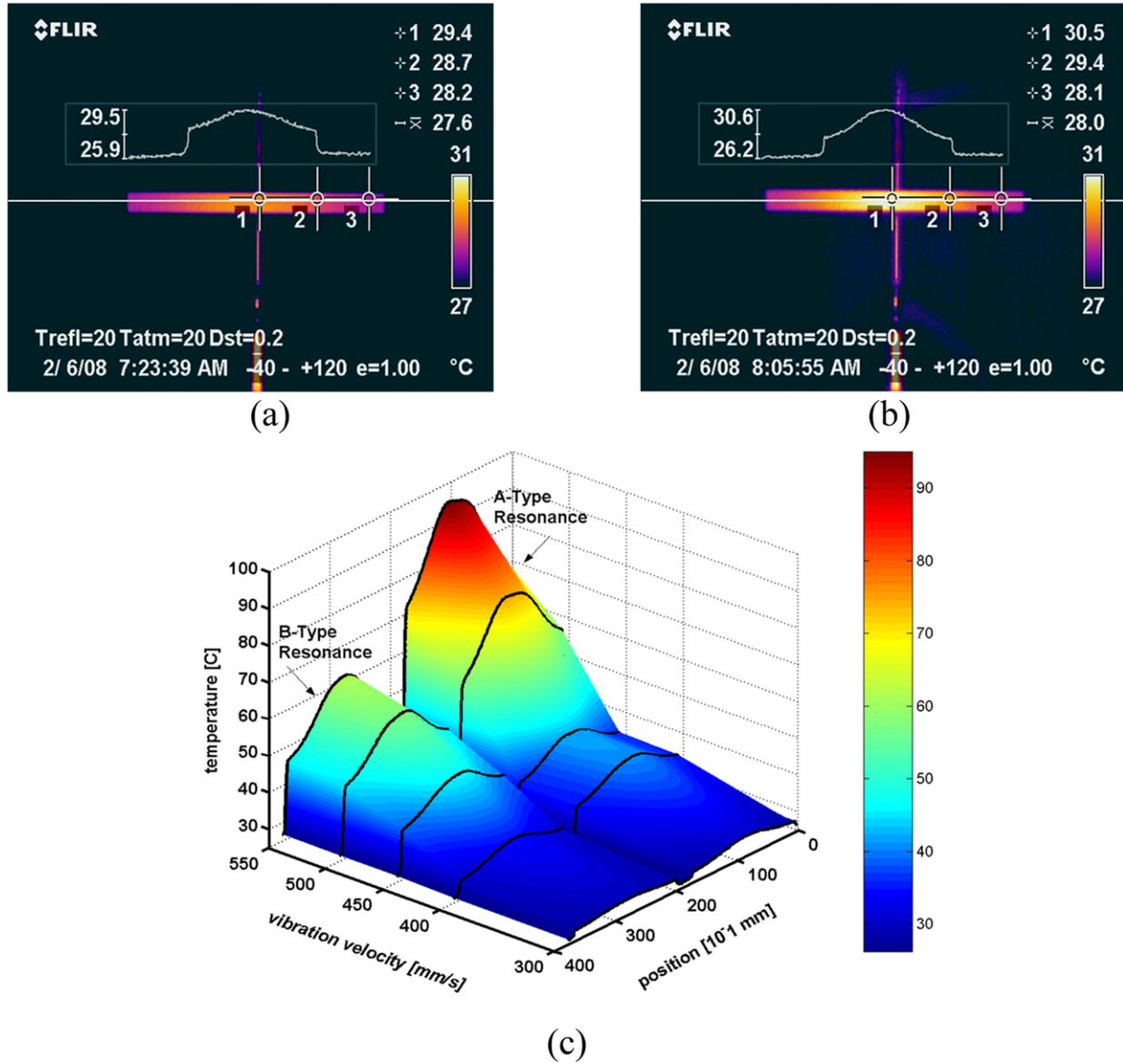


Fig. 11 Temperature variations in a PZT plate specimen observed by a pyroelectric infrared camera. The specimen was driven at the antiresonance (a) and resonance frequency (b). (c) Numerical temperature profile for the A- and B-type resonance modes.

distribution profile for the k_{31} specimen is shown in Fig. 12(b), which can be used for calculating the total thermal dissipation energy g_h . A small temperature dent around $x = 0$ (i.e., plate center) originated from the heat dissipation by the center specimen-holding rod conduction was neglected in the curve-fitting simulation.

Let us adopt the most general definition of the “mechanical quality factor Q_m ” as

$$Q_m = 2\pi \frac{\text{Energy Stored/Cycle}}{\text{Energy Lost/Cycle}}, \quad (76)$$

In our scenario, the Q_m is defined as the ratio of elastic energy of an oscillator to the power being dissipated by elastic mechanisms

$$Q_m = 2\pi f_r \frac{U_e}{P_d}, \quad (77)$$

where U_e is the maximum stored mechanical energy and P_d is the dissipated power, measured in this experiment by heat generation measurements through temperature, under a supposition $P_d =$ Electrically spent energy (Shekhani and Uchino, 2014a,b). Because the compliance of a piezoelectric material has non-linearity, the maximum kinetic energy is used to define the stored energy term. For a longitudinally vibrating rod, the kinetic energy as a function of displacement, u_x , is

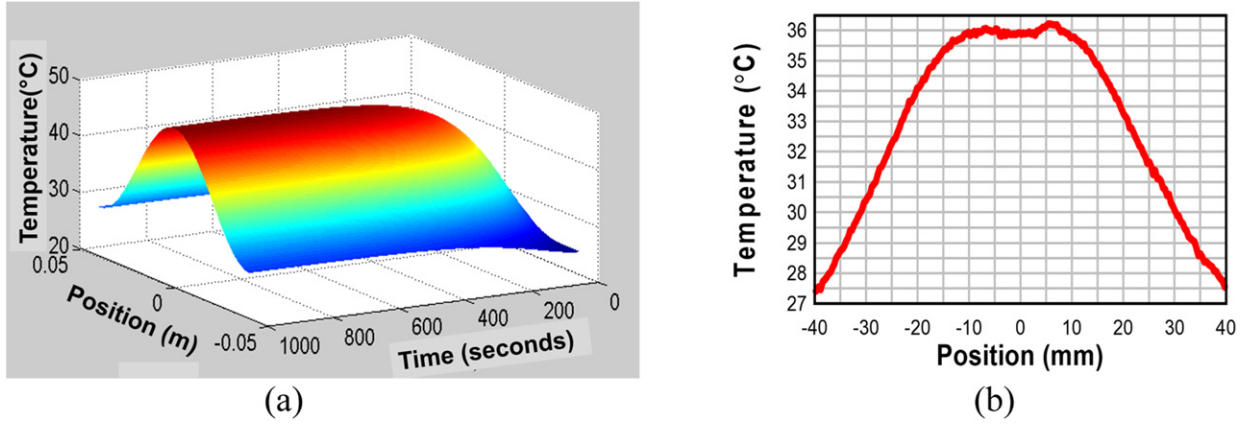


Fig. 12 (a) Temperature distribution profile change with time after driving. (b) The saturated temperature distribution profile for k_{31} specimen with $80 \times 14 \times 2 \text{ mm}^3$.

$$U_e = \frac{1}{2} A \int_{-\frac{L}{2}}^{\frac{L}{2}} \rho \left(\frac{\partial u_x}{\partial t} \right)^2 dx \quad (78)$$

Using the geometry of Fig. 4 and assuming sinusoidal strain (Eq. (35)) at a frequency near the fundamental resonance, the spatial vibration can be described as

$$u_x(x, t) = V_{rms} \sqrt{2} \sin\left(\frac{\pi x}{L}\right) \sin(2\pi f t) \quad (79)$$

The maximum kinetic energy can be calculated as

$$U_e = \frac{1}{2} A \int_{-\frac{L}{2}}^{\frac{L}{2}} \rho \left(V_{rms} \sqrt{2} \sin\left(\frac{\pi x}{L}\right) \right)^2 dx = V_{rms}^2 \rho A \frac{L}{2} \quad (80)$$

Regarding P_d , because the strain/stress distribution is almost sinusoidal, we suppose volumetric heat generation is provided by

$$u_G(x) = u_G \cos^2\left(\frac{\pi x}{L}\right) \quad (81)$$

The dissipated power due to convection and radiation is equal to the heat generation at steady state, so P_d can be expressed as

$$P_d = A \int_{-\frac{L}{2}}^{\frac{L}{2}} u_G \cos^2\left(\frac{\pi x}{L}\right) dx = \frac{1}{2} u_G A L. \quad (82)$$

Thus, substituting these expressions into Eq. (77), the quality factor in terms of heat generation and rms vibration velocity can be formed

$$Q_m = 2\pi f_r \times \frac{\rho V_{rms}^2}{u_G}. \quad (83)$$

Note that the Q_m does not depend explicitly on geometrical terms, as is expected if the mode of vibration is known. We see that if the vibration velocity is increased, the heat generation must also increase. Although this derivation is specific to longitudinal vibration of a rod at fundamental resonance, it can easily be extended to higher modes of vibration and also other structures such as disks. This can be accomplished by altering the shape of the heat generation distribution and the vibration velocity distribution and then reinvoking the definition of the mechanical quality factor. This is the unique approach to determine the mechanical quality factor with using merely the thermal data, without using any electrical energy information.

Shekhani *et al.* (measured the admittance spectrum on the above PZT sample ($80 \times 14 \times 2 \text{ mm}^3$) with the resonance frequency at 20.04 kHz at room temperature, and obtained $Q_m = 507$ by a 3-dB-down method on an admittance spectrum. Then, the sample was excited under the vibration velocity of 400 mm/s for 30 s, which corresponds to the heat dissipation of 11.6 W/m^2 . Fig. 13(a) shows the Q_m obtained at three frequencies slightly above the resonance frequency (20.04 kHz) (Shekhani and Uchino, 2014a). The Q_m values around 550 agree with the extrapolated values from the above 507. Thus, we can conclude that this thermal method can determine the Q_m reasonably at any frequency (not only the resonance and the antiresonance frequencies!). An increase of Q_m with increasing the frequency is obvious, which will be discussed further in Section “High Power Piezoelectric Characterization System (HiPoCS)”.

Temperature distribution profile versus thermal diffusivity

Fig. 13(b) demonstrates the saturated temperature distribution profile difference between two compositions, PZT-5 H and PZT-19 under the same vibration velocity operating condition. These two compositions exhibit significant difference in thermal conductivity: 0.14 W/m K versus 2 W/m K (more than 10 times difference). The profile curve of PZT-5 H fits a sinusoidal line

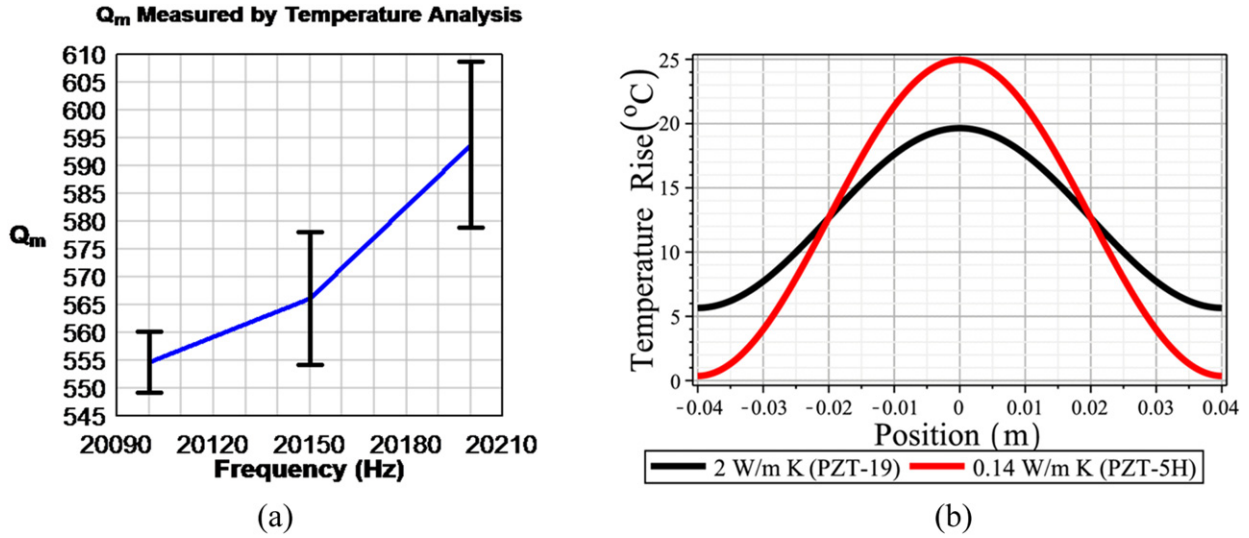


Fig. 13 (a) Change in Q_m with frequency ($f_r \approx 20.006 \text{ kHz}$). (b) Saturated temperature distribution profile difference between PZT-5 H and PZT-19.

($g_h \cos^2(\frac{\pi x}{L})$) beautifully, while PZT-19 shows considerable edge temperature rise. You can understand easily that this profile difference is originated primarily from the “thermal conductivity or diffusivity” difference. Taking the total thermal energy dissipated from the specimen by integrating the temperature rise with respect to the position coordinate, we can expect a similar mechanical quality factor Q_m value for these two samples. However, you can notice that the peak temperature at the nodal point is significantly lower for the larger thermal conductivity material, which means we can excite the vibration more under higher voltage for the PZT-19, because the “maximum vibration velocity” v_{max} is defined by the highest temperature rise 20°C above room temperature. Pb-free piezoceramics such as (Na,K)NbO₃-based materials show much higher maximum vibration velocity than the PZT’s (Gurdal *et al.*, 2013). Much larger thermal conductivity in the NKN-based material than the PZT’s [$\kappa = 3.10 \text{ W/mK}$] in comparison with $\kappa = 1.25$ in hard PZT: unreported data] may also contribute to this superior high-power performance in NKN-ceramics. Section “High Power Piezoelectric Characterization System (HiPoCS)” describes this high-power figure of merit v_{max} in details.

High Power Piezoelectric Characterization System (HiPoCS)

There are various methods for characterizing loss factors and high-power characterizations in the piezoelectric materials, in addition to the thermal analysis method introduced in Section “Temperature distribution profile change with time”. Pseudo-static, admittance spectrum, and transient/burst mode methods. The admittance/impedance spectrum method is further classified into (1) constant voltage, (2) constant current, and (3) constant vibration velocity methods. Piezoelectric resonance can be excited by either electrical or mechanical driving, as shown in Fig. 14. In the k_{31} mode, as long as the surface is electroded, the sound velocity is v^E originated from s_{11}^E , while no-electrode, they are v^D and s_{11}^D . A short-circuit condition realizes the resonance and an open-circuit condition provides the antiresonance mode. In order to measure the D -constant parameters (s_{11}^D and its extensive elastic loss $\tan\phi$) directly, we need to use a non-electrode sample under mechanical driving methods.

Loss Measuring Technique I – Pseudo-Static Method

We can determine “intensive dissipation factors”, $\tan\delta'$, $\tan\phi'$, and $\tan\theta'$, separately from (a) D versus E (stress free), (b) x versus X (short-circuit), (c) x versus E (stress free) and (d) D versus X (short-circuit) curves (see Fig. 1). Using a stress applying jig, Zheng *et al.* measured the x versus X and D versus X relationships on a “soft PZT” based multilayer (ML) actuator to obtain intensive loss factors, $\tan\delta'$, $\tan\phi'$, and $\tan\theta'$ as a function of electric field or compressive stress, through Eqs. (6b), (7b), 8(b) and (9b) (Zheng *et al.*, 1996). The reader needs to understand that different from the dielectric and elastic losses, the piezoelectric loss cannot be determined directly from the hysteresis loss, but a sort of “hidden loss” always accompanied by other losses. Using this classic measurement, we reported that piezoelectric loss $\tan\theta'$ is not negligibly small as believed by the previous researchers, but rather large compared to the dielectric and elastic losses; $\tan\theta' (= 0.08) > \frac{1}{2} [\tan\delta' (= 0.06) + \tan\phi' (= 0.08)]$. Then, using the K -matrix (Eqs. (31a) and (31b)), we calculated the “extensive losses”. The results indicate that the magnitude of the piezoelectric loss $\tan\theta$ is comparable to the dielectric and elastic losses, and increase gradually with the field or stress; now $\tan\theta (= 0.05) < \frac{1}{2} [\tan\delta (= 0.05) + \tan\phi (= 0.07)]$. We also point out that the “extensive dielectric loss $\tan\delta$ increases significantly with an increase of the intensive parameter, i.e., the applied electric field, while the extensive elastic loss $\tan\phi$ is rather insensitive to the intensive parameter, i.e., the applied compressive stress”. When similar

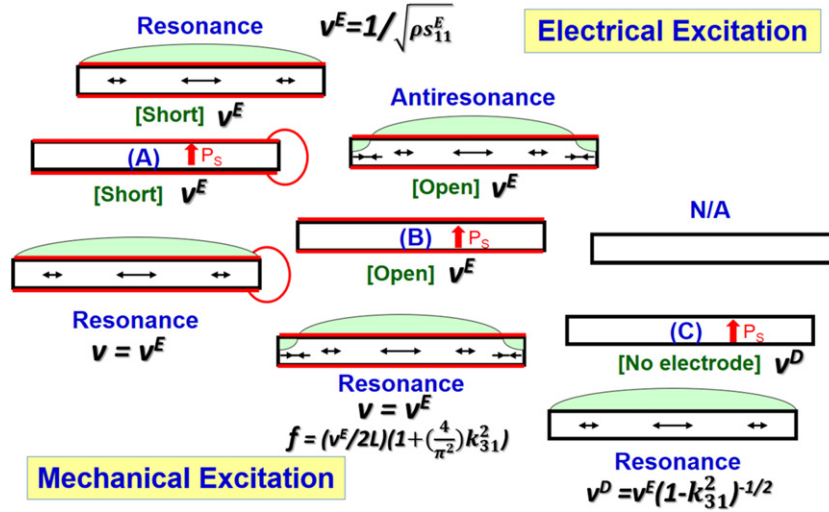


Fig. 14 Resonance and antiresonance mode excitation under electrical or mechanical driving methods.

measurements are conducted under constrained conditions; that is, D versus E under a completely clamped state, and x versus X under an open-circuit state, respectively, the reader may expect smaller hysteresis, that is, extensive losses, $\tan\delta$ and $\tan\phi$, theoretically. However, they are rather difficult in practice because of the migrating charge compensation on the specimen surface.

Loss Measuring Technique II – Admittance/Impedance Spectrum Method

Since the pseudo-static method equipment introduced in the previous section is a little difficult to set up for lay customers, we introduce the electric admittance/impedance measuring methods in this section.

Resonance under constant voltage drive (HiPoCS I)

Because commercially available “Impedance Analyzer” did not generate high voltage/current for measuring the high-power piezoelectric performance, Uchino (as an NF Corporation Deputy Director, Japan) commercialized “Frequency Response Analyzer” (500 V, 20A, 1 MHz maximum) from NF Corporation, Japan. Uchino *et al.* (1989) reported the existence of the critical threshold voltage and the maximum vibration velocity for a piezoelectric, above which the piezoelectric drastically increases the heat generation and becomes a ceramic heater. Though this measurement technique is simple yet sophisticated, there have been problems in heat generation in the specimen around the resonance range, further in significant distortion of the admittance frequency spectrum when the sample is driven by a constant voltage, due to the nonlinear behavior of elastic compliance at high vibration amplitude. Refer to Ref (Uchino, 2022). for the analytical discussion on the elastic nonlinearity. Fig. 15(a) exemplifies the problem, where the admittance spectrum is skewed with a jump around the maximum admittance point. Thus, we cannot determine the resonance frequency nor the mechanical quality factor precisely from these skewed spectra. Thus, HiPoCS first version did not have a capability to measure the piezoelectric loss.

Resonance under constant current drive (HiPoCS II)

In order to escape from the problem with a constant voltage measurement, we proposed a constant current measurement technique (Hirose *et al.*, 1995). Since the vibration amplitude is primarily proportional to the driving current (not the voltage) at the resonance, a constant current condition guarantees almost constant vibration amplitude through the resonance frequency region, escaping the spectrum distortion due to the elastic non-linearity. As demonstrated in Fig. 15(b), the spectra exhibit symmetric curves, from which we can determine the resonance frequency and the mechanical quality factor Q_A precisely.

Although the traditional constant voltage measurement was improved by using a constant current measurement method, the constant current technique (HiPoCS (II)) is still limited to the vicinity of the resonance. In order to identify a full set of high-power electromechanical coupling parameters and the loss factors of a piezoelectric, both resonance and antiresonance vibration performance (in particular, Q_A and Q_B) should be precisely measured simultaneously. Basically, Q_A can be determined by the constant current method around the resonance (A-type), while Q_B should be determined by the constant voltage method around the antiresonance (B-type). The mechanical quality factor Q_m (or the inverse value, loss factor $\tan\phi$) is obtained from $Q_m = \frac{\omega_R}{2\Delta\omega}$, where $2\Delta\omega$ is a full width of the $1/\sqrt{2}$ (i.e., 3 dB down) of the maximum admittance value at ω_R . HiPoCS (II) improved the capability for measuring the mechanical quality factor Q_m at the resonance region, but did not provide information on the piezoelectric loss $\tan\theta'$ easily because we need to switch the measuring systems between constant-current and constant-voltage types.

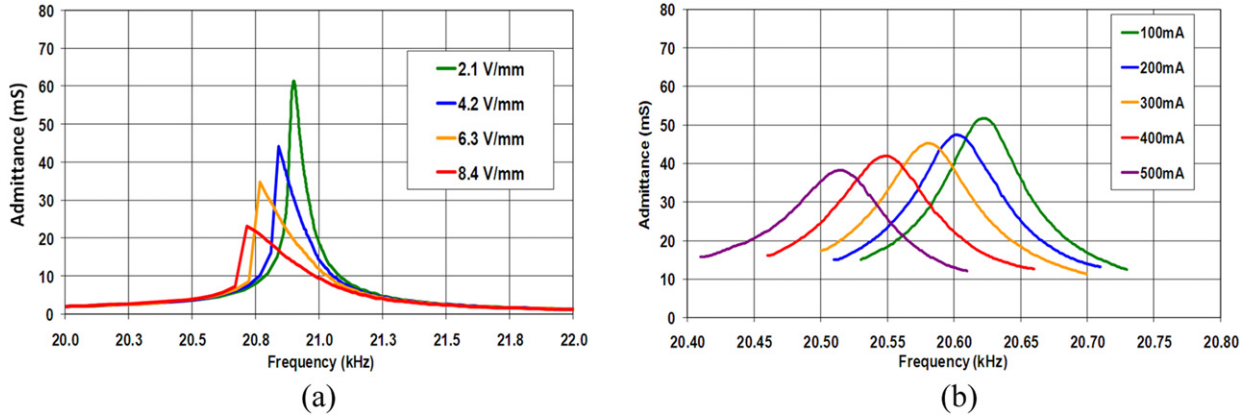


Fig. 15 Admittance frequency spectra under (a) constant voltage, and (b) constant current condition. (Data taken by Michael R. Thibeault, The Penn State Univ.).

We reported the degradation of the mechanical quality factor Q_m with increasing electric field and vibration velocity (Hirose *et al.*, 1995). Fig. 16 shows the vibration velocity dependence of the mechanical quality factors Q_A and Q_B , and corresponding temperature rise for A (resonance) and B (antiresonance) type resonances of a longitudinally vibrating PZT ceramic transducer through the transverse piezoelectric effect d_{31} (the sample size is inserted) (Uchino and Hirose, 2001). Two comments are provided: (1) The piezoelectric k_{31} -type rectangular plate with 40 mm long was occasionally used, because this structure is a sort of standard size for the piezoelectric transformer designs; (2) In order to evaluate the mechanical vibration level, we introduced the “vibration velocity” at the rectangular plate tip, rather than the “vibration displacement”, because the displacement is size-dependent, while the velocity is not. Fig. 16 exhibits that Q_m is almost constant for a small electric field/vibration velocity, but above a certain vibration level Q_m degrades drastically, where temperature rise starts to be observed (Uchino and Hirose, 2001). The “maximum vibration velocity” is defined at the velocity where a 20°C temperature rise (from the human safety regulation) at the nodal point (i.e., maximum temperature point) from room temperature occurs. Note that even if we further increase the driving voltage/field, additional energy will convert to merely heat (i.e., PZT becomes a ceramic heater!) without increasing the vibration amplitude. Thus, the reader can understand that the “maximum vibration velocity” is a sort of material’s constant which ranks the high-power performance. Note that most commercially available hard PZTs exhibit the maximum vibration velocity around 0.3 m/sec, which corresponds to roughly 5 W/cm³ (i.e., 1 cm³ PZT can generate maximum 5 W mechanical energy).

When we compare the change trends in Q_A and Q_B , Q_B is higher than Q_A in all vibration level (This is true in PZT’s). Accordingly, the heat generation in the A-type (resonance) mode is higher than the B-type (antiresonance) mode under the same vibration velocity level (in other words, the maximum vibration velocity is higher for Q_B than for Q_A), the situation of which was already shown in Fig. 11.

The sudden degradation of the mechanical quality factor is explained by superposing the change trends of elastic and dielectric losses. Note that the Q_m is the inverse of intensive elastic loss $\tan\phi'$, and that it is expressed by the extensive losses as $\tan\phi' = \left(\frac{1}{1-k^2}\right)[\tan\phi + k^2(\tan\delta - 2\tan\theta)]$. We speculate the extensive mechanical loss $\tan\phi$, mainly related to the 90° (or non-180°) domain wall motion, is insensitive to the vibration velocity; while the extensive dielectric loss $\tan\delta$, related to 180° domain wall motion, increases significantly around a certain critical vibration velocity, according to Uchida-Ikeda model introduced in Section “Loss Mechanisms In Piezoelectrics”. This notion was already supported experimentally in Section “Loss Measuring Technique I – Pseudo-Static Method”, in which “extensive dielectric loss $\tan\delta$ increases significantly with an increase of the applied electric field, while the extensive elastic loss $\tan\phi$ is rather insensitive to the applied compressive stress”. Thus, the resonance loss at a small vibration velocity is mainly determined by the extensive mechanical loss which provides a high mechanical quality factor Q_m , and with increasing vibration velocity, the extensive dielectric loss contribution increases exponentially. After $\tan\delta$ exceeds $\tan\phi$ around the maximum vibration velocity v_{max} , we start to observe heat generation. As derived in Eqs. (9b) and (8b), the piezoelectric loss is always coupled with either dielectric or elastic losses as $(\tan\delta - 2\tan\theta)$ above, originated from an electromechanical coupling loss $-(2\tan\theta - \tan\delta - \tan\phi)$.

Resonance/antiresonance under constant vibration velocity (HiPoCS III)

Zhuang and Uchino derived an expansion-series approximation of the mechanical quality factors at both resonance and anti-resonance modes, as introduced in Section “Admittance around resonance and antiresonance”, and finally obtained a useful Uchino-Zhuang formula (Zhuang *et al.*, 2009a, 2010), Eq. (63):

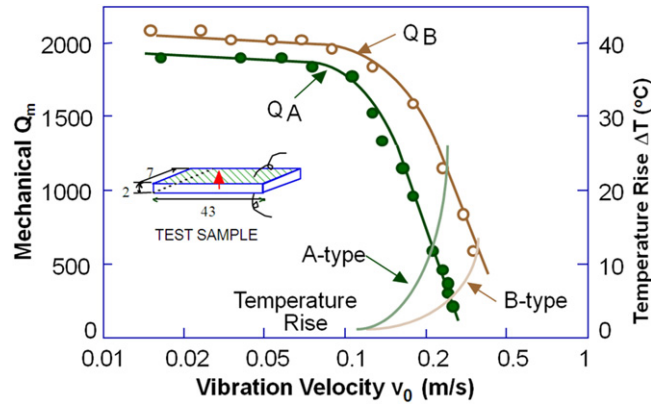


Fig. 16 Vibration velocity dependence of the mechanical quality factors Q_A and Q_B and corresponding temperature rise for A (resonance) and B (antiresonance) type resonances of a k_{31} PZT ceramic transducer (the sample size is inserted). Reproduced from Uchino, K., Hirose, S., 2001. Loss mechanisms in piezoelectrics: How to measure different losses separately. IEEE-UFFC Trans. 48, 307–321.

$$\left\{ \begin{array}{l} \frac{1}{Q_{A,31}} = \tan\phi'_{11} \\ \frac{1}{Q_{B,31}} = \frac{1}{Q_{A,31}} - \frac{1}{1 + \left(\frac{1}{k_{31}} - k_{31}\right)^2 \Omega_B^2} \left(2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11}\right) \end{array} \right\}$$

The key is that if we precisely measure both Q_A and Q_B values, the information on the piezoelectric loss $\tan\theta'$ can be obtained. Thus, we proposed a simple, easy and user-friendly method to determine the piezoelectric loss factor $\tan\theta'$ in k_{31} mode through admittance/impedance spectrum analysis:

- (1) Obtain $\tan\delta'$ from an impedance analyzer or a capacitance meter at a frequency away (lower range) from the resonance/antiresonance range;
- (2) Obtain the following parameters experimentally from an admittance/impedance spectrum around the resonance (A-type) and antiresonance (B-type) range (3 dB bandwidth method): ω_a , ω_b , Q_A , Q_B and the normalized frequency $\Omega_b = \frac{\omega_b L}{2v}$;
- (3) Obtain $\tan\phi'$ from the inverse value of Q_A (quality factor at the resonance) in the k_{31} mode;
- (4) Calculate electromechanical coupling factor k_{31} from the ω_a and ω_b with the IEEE Standard equation in the k_{31} mode: $\frac{k_{31}^2}{11k_{31}^2} = \frac{\pi\omega_b}{2\omega_a} \tanh\left[\frac{\pi(\omega_b - \omega_a)}{2\omega_a}\right]$;
- (5) Finally obtain $\tan\theta'$ from the above Eq. (63) in the k_{31} mode.

As long as we obtain ω_a , ω_b , Q_A , Q_B even from the Burst Drive method introduced in the next section, the above procedure can also be used.

In order to identify both mechanical quality factors Q_A and Q_B precisely for adopting the above-mentioned user-friendly methodology, both resonance and antiresonance vibration performance should be measured simultaneously. Basically, Q_A can be determined by the “constant current method” around the resonance (A-type), while Q_B should be determined by the “constant voltage method” around the antiresonance (B-type). Thus, we developed HiPoCS Version III shown in Fig. 17, which is capable of measuring the impedance/admittance curves by keeping the following various conditions: (1) constant voltage, (2) constant current, (3) “constant vibration velocity” of a piezoelectric specimen, and (4) constant input power (Ural et al., 2009). In addition, the system is equipped with an infrared image sensor to monitor the heat generation distributed in the test specimen.

Fig. 18 shows an interface display of HiPoCS Ver. III, demonstrating a rectangular k_{31} plate measurement under a “constant vibration velocity” condition. In order to keep the vibration velocity constant (i.e., stored/converted mechanical energy is constant) the current and voltage are changed automatically in the system; the current is almost constant and the voltage is minimized at the resonance, while the voltage is almost constant and the current is minimized at the antiresonance frequency. The apparent power is shown in the top of Fig. 18, which clearly indicates that the antiresonance operation requires less power than the resonance mode for generating the same vibration velocity (or stored mechanical energy) (Ural et al., 2009). We can conclude that the PZT transducer should be operated at the antiresonance frequency, rather than the resonance mode, if we consider the energy efficiency.

Real electric power method (HiPoCS IV)

Because the conventional admittance spectrum method can provide the mechanical quality factors only at two frequency points (i.e., resonance Q_A and antiresonance Q_B), we had a frustration for knowing the Q_m at any frequency. A unique methodology for characterizing the quality factor in piezoelectric materials has been developed in the ICAT by utilizing real electrical power measurements (including the phase lag), e.g., $P = V \cdot I \cdot \cos\phi$, rather than the apparent power $V \cdot I$, which is demonstrated in Fig. 18 Top (Shekhani and Uchino, 2014b). As explained in the derivation process of Eq. (83), we can obtain the mechanical quality factor Q_m from the ratio of mechanical stored energy over the dissipated input energy, i.e., real electrical power, under the

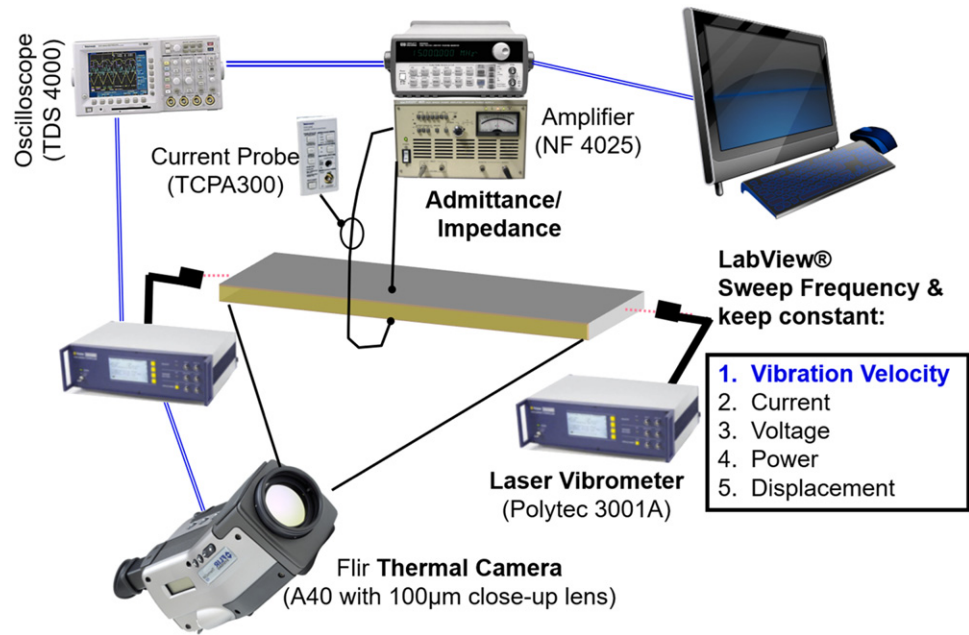


Fig. 17 Setup of HiPoCS version III.

Constant Vibration Velocity Sweep

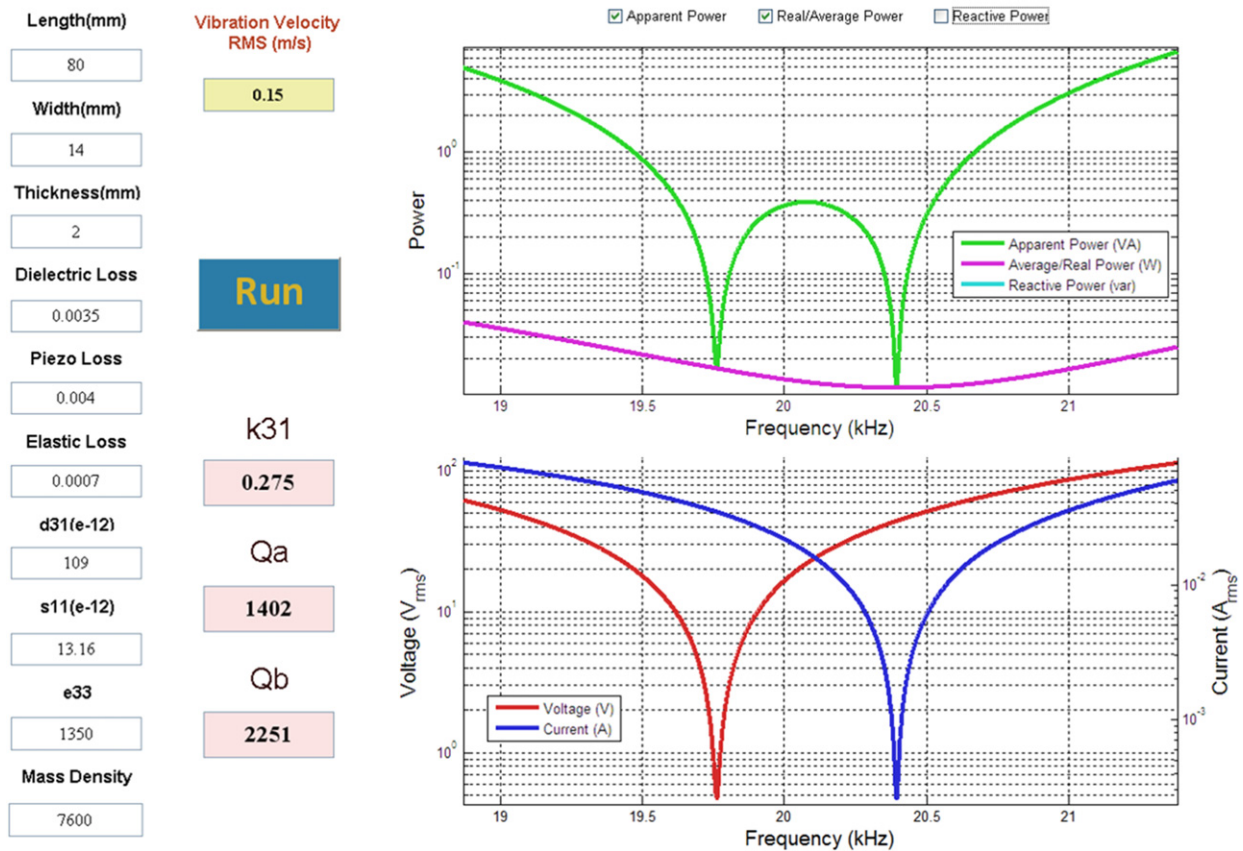


Fig. 18 Voltage and current change with frequency under the constant vibration velocity condition.

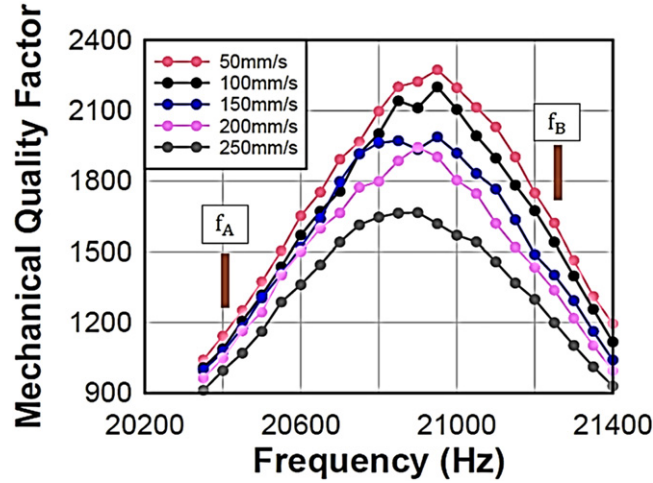


Fig. 19 Mechanical quality factor measured using real electrical power for a Hard PZT APC 851 k_{31} plate.

suppositions: (1) at equilibrium the power input is the power lost as heat, and (2) the stored mechanical energy can be predicted using the known vibration velocity of a particular mode shape. We can derive the following equation from these concepts, which allows the calculation of the mechanical quality factor at any frequency from the real electrical power (P_d) and tip rms vibration velocity (V_{rms}) measurements for a longitudinally vibrating piezoelectric resonator (k_t, k_{33}, k_{31}):

$$Q_m = 2\pi f_r \times \frac{\frac{1}{2}\rho V_{rms}^2}{P_d/(Lwb)} \quad (84)$$

The change in mechanical quality factor was measured for a hard PZT (APC 851) ceramic plate (k_{31}) under various constant vibration velocity conditions (50–250 mm/s rms tip vibration velocity) (i.e., stored mechanical energy constant). The experimental key in the HiPoCS Ver. IV is to determine the phase difference ϕ precisely to obtain the $\cos\phi$ value. The frequency spectra of the mechanical quality factor Q_m are shown in Fig. 19 for various vibration velocities. The quality factor obtained at the resonance is within 2% agreement with results from the impedance spectrum method (3 dB-down bandwidth). Q_m at the antiresonance frequency (i.e., Q_B) is higher than Q_A at the resonance, as expected. Furthermore, this technique reveals the behavior of the mechanical quality factor at any frequency between the resonance and the antiresonance frequencies, and very interestingly, the mechanical quality factor reaches a maximum value between the resonance and the antiresonance frequency, the point of which may suggest the optimum condition for the transducer operation merely from an efficiency viewpoint. Note that the maximum Q_m frequency point shifts to a lower frequency with increasing the vibration velocity, which may be originated from the different change of three dielectric, elastic and piezoelectric loss factors with the vibration velocity. The microscopic origin needs to be elucidated for understanding the behavior of piezoelectric material properties under high power excitation.

Determination methods of the mechanical quality factor

We provide remarks on the precise determination method of the mechanical quality factor. So far we introduced the “3 dB up/down method” on the admittance/impedance magnitude spectrum, as shown in Fig. 5. We occasionally use the “quadrantal frequency method” for more precise determination. The real and imaginary admittances (that is G versus B of $Y^* = G + jB$) of the k_{31} mode are plotted as its admittance circle [Fig. 20(a)]. The admittance circle emphasizes the admittance and phase change just around the resonance range. On the contrary, when we plot the impedance circle [Fig. 20(b), $Z^* = R + jX$], we can obtain the information around the antiresonance range.

The resonance frequency is defined by ω_R , the most right on the admittance circle, while the antiresonance frequency is defined by ω_A , the intersect between the admittance circle and the susceptance $B = 0$, or the most right on the impedance circle (the reader can understand this is much easier). Popularly used maximum and minimum frequencies of the admittance magnitude, ω_m and ω_n are not exactly the resonance and antiresonance frequency. Note $\omega_m < \omega_R = \omega_0 < \omega_A < \omega_n$. From Fig. 20, the reader can understand that the top and bottom points of the admittance (or impedance) circle exhibit the $1/\sqrt{2}$ (or 3 dB down) of Y , which are called “quadrantal frequencies”. Using these ω'_1 and ω'_2 , we obtain

$$Q_A = \omega_R/(\omega'_2 - \omega'_1) \quad (85a)$$

By fitting the circle to a slightly-distorted measured experimental data, we can obtain rather precise Q_A in comparison with the 3 dB down method. In particular, the impedance circle provides the antiresonance Q_B information.

$$Q_B = \omega_A/(\omega'_4 - \omega'_3) \quad (85b)$$

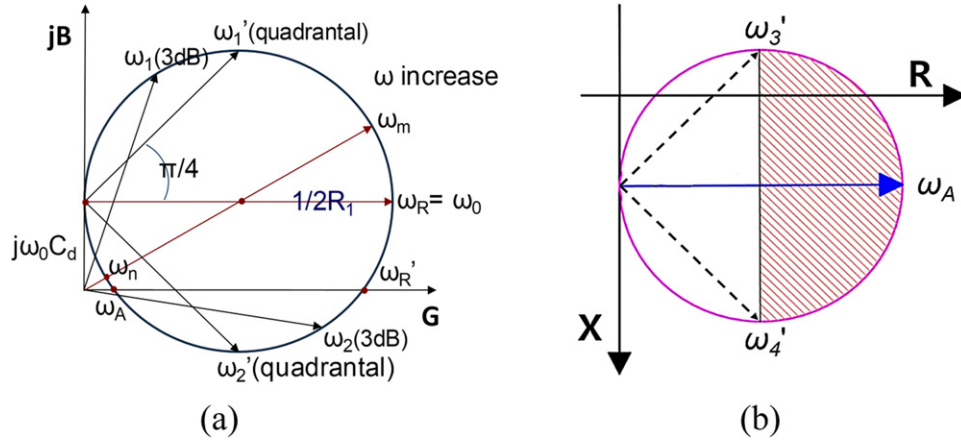


Fig. 20 (a) Admittance circle. (b) Impedance circle.

Loss Measuring Technique III – Transient/Burst Drive Method

The transient/burst drive methods are “mechanical excitation” method for characterizing the high-power piezoelectric performances by measuring the ring-down mechanical vibration decay. As Fig. 14 indicates, depending on the electrical boundary condition, short-circuit or open-circuit, we can obtain the resonance or antiresonance behavior, respectively.

Pulse drive method

The pulse drive method is a simple method for measuring high voltage piezoelectric characteristics, developed in the ICAT/Penn State in the early 1990s. By applying a step electric field to a piezoelectric sample, the transient vibration displacement corresponding to the desired mode (extensional, bending etc.) is measured under a short-circuit condition. The resonance period, stabilized displacement and damping constant are obtained experimentally, from which the elastic compliance, piezoelectric constant, mechanical quality factor and electromechanical coupling factor can be calculated. Using a rectangular piezoelectric ceramic plate (length: L ; width: w ; and thickness: b ; poled along the thickness. Fig. 4), we explain how to determine the electromechanical coupling parameters k_{31} , d_{31} and Q_m . The density ρ , permittivity ϵ_{33}^X , and size (L , w , b) of the ceramic plate must be known prior to the experiments.

- (1) From the stabilized displacement, we obtain the piezoelectric coefficient d_{31} :

$$D_s = d_{31}EL \quad (86)$$

- (2) From the ringing period, we obtain the elastic compliance s_{11}^E :

$$T_0 = \frac{2L}{v} = 2L\sqrt{\rho s_{11}^E} \quad (87)$$

3. From the damping constant τ , which is determined by the time interval to decrease the displacement amplitude by $1/e$, we obtain the mechanical quality factor Q_m :

$$Q_m = \frac{1}{2}\omega_0\tau,$$

where the resonance angular frequency $\omega_0 = 2\pi/T_0$.

4. From the piezoelectric coefficient d_{31} , elastic compliance s_{11}^E , and permittivity ϵ_3 , we obtain the electromechanical coupling factor k_{31} :

$$k_{31} = d_{31}/\sqrt{\epsilon_0\epsilon_3s_{11}^E} \quad (89)$$

On the other hand, the antiresonance Q_m can be obtained as follows: By removing a large electric field suddenly from a piezoelectric sample, and keeping the open-circuit, the transient vibration displacement corresponding to the antiresonance mode. Although the experimental accuracy of the pulse drive method is not very high, the simple setup is attractive especially for its low cost. Moreover, unlike the resonance/antiresonance spectrum method, this technique requires only one voltage pulse during the measurement, and thus does not generate heat (i.e., temperature effect can be eliminated). Thus, the electric field dependence of piezoelectricity can be measured.

Burst mode method (HiPoCS V)

Because a continuous HiPoCS admittance/impedance spectrum characterization of high-power piezoelectrics is inevitably associated with the temperature rise around the resonance and antiresonance modes in particular (even under constant vibration

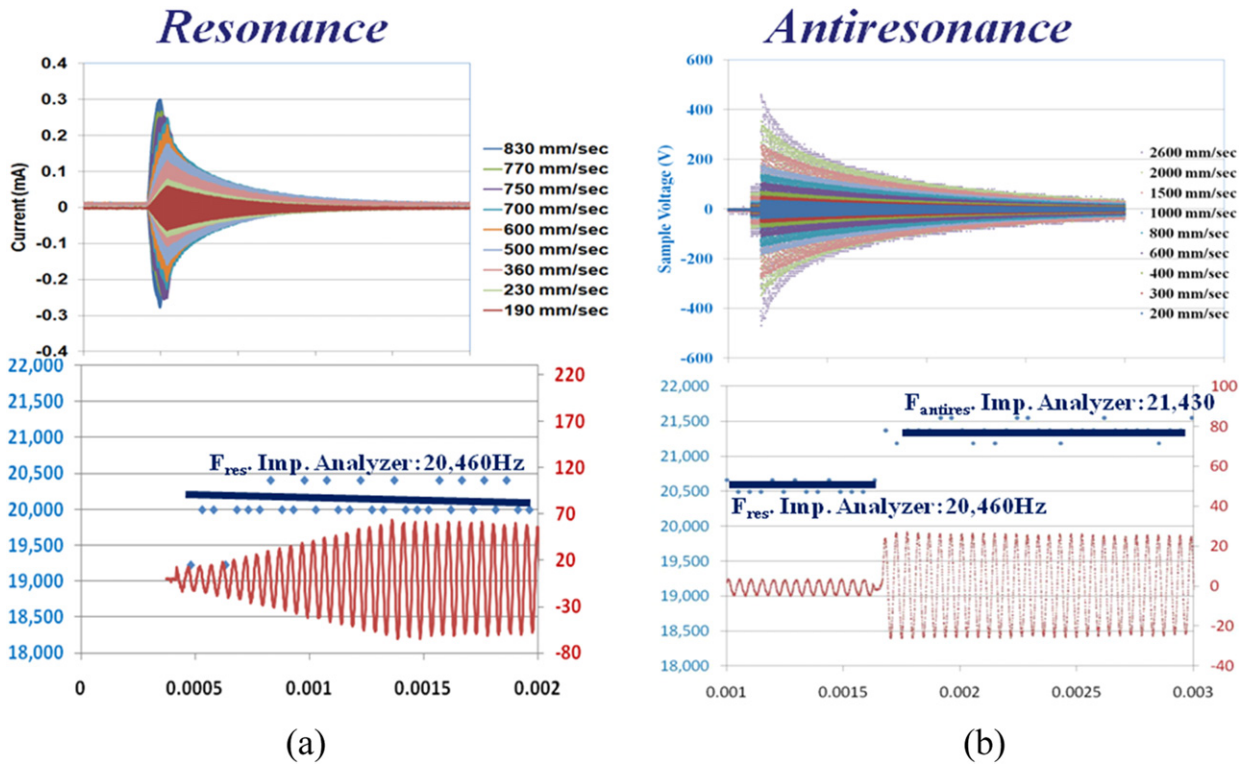


Fig. 21 Vibration ring-down characteristics for the short- (a) and open-circuit condition (b). Note the sudden change of the ringing frequency for the open-circuit.

velocity conditions), pure vibration amplitude dependence of the Q_M cannot be discussed without removing the temperature influence. In order to eliminate the temperature rise effect, the burst method can be chosen (extended from the pulse drive method). In this method, different from the “pulse drive method”, the initial mechanical excitation is made by the resonance frequency, so that significantly large vibration velocity can be obtained under small voltage. Due to the “burst mode” (~ 1 msec), the internally generated heat is close to none (less than 0.1°C), and observations would be a direct function of the ambient temperature on piezoelectric properties. This technique was reported systematically on the resonance mode by Umeda *et al.* for determining the equivalent circuit parameters of a piezoelectric transducer (Umeda *et al.*, 1999a). It was thereafter adapted to measure the properties of piezoelectric ceramic specimens (Takahashi *et al.*, 1999; Umeda *et al.*, 1999b).

The author's group introduced an open-circuit system, in addition to a short-circuit condition, which functions immediately after the resonance burst drive (only for 1 msec) without generating heat, which generates the ring-down of vibration amplitude for the antiresonance and resonance mode, respectively. Fig. 21 illustrates the results for the short- and open-circuit (Shekhani *et al.*, 2016). First, we excited a k_{31} rectangular plate (80 mm L) at its resonance frequency (~ 20 kHz) for 1–2 msec (short period without generating heat higher than 0.1°C). Then, disconnecting the power supply for 50 μsec , we adopted short-circuit or open-circuit condition with mechanical latching relay. In the short-circuit, the current and vibration velocity are proportional, the decay rate of which provides the mechanical quality factor Q_A (resonance), while in the open-circuit, the voltage and end displacement are proportional, the decay rate of which gives the Q_B (antiresonance). Note that resonance to antiresonance frequency jump in the Fig. 21(b) owing to a sudden electrical open-circuit from the initial resonance excitation. Regarding the modification from HiPoCS Ver. IV, a short-circuit and open-circuit relays were integrated. With the new blocking circuit added to our burst method characterization with the HiPoCS, we can monitor the mechanical quality factor drop (via high induced voltage) also in the antiresonance condition.

We introduced first the voltage factor (B_{31}) (defined by the ratio (voltage/displacement) under the open-circuit condition), in addition to the conventional the force factor (A_{31}) (defined by the ratio (current/vibration velocity) under the short-circuit condition) in terms of material properties and specimen geometry from the constitutive equations for the k_{31} piezoelectric specimen (Shekhani *et al.*, 2016). The force factor is related to the piezoelectric stress coefficient (e_{31}), the analysis of which has been presented previously by Takahashi *et al.* (1999). On the contrary, the voltage factor (B_{31}) is related with the converse piezoelectric coefficient (h_{31}), which has not been applied nor analyzed in bulk piezoceramics in the antiresonance condition so far.

We consider again the k_{31} mode specimen geometry in Fig. 4. The derivations assume a rectangular plate with $b \ll w \ll L$, fully electroded, and poled along the thickness. Another assumption is that most of the vibration occurs in the length direction, traditionally corresponding to the x direction ($x = 0$ is at the plate center in the following analysis). In general, the mode shape of

a piezoelectric resonator with stress free boundary conditions, undergoing vibration in 1-D with losses, and having finite displacement can be described as

$$u(x, t) = u_0 f(x) \sin \omega t, \quad (90)$$

where $f(x)$ is a function symmetric about the origin normalized to the displacement at the ends of the piezoelectric resonator, where $f(x) = 0$. Then, according to the fundamental theorem of calculus in terms of strain ($\partial u / \partial x$), we obtain:

$$\int_{-L/2}^{L/2} \frac{\partial u}{\partial x} dx = u(L/2, t) - u(-L/2, t) = 2u_0 \sin \omega t. \quad (91)$$

The constitutive equation describing the electric displacement of a piezoelectric k_{31} resonator is

$$D_3(t) = e_{31} \frac{\partial u}{\partial x} + \epsilon_{33}^{x_1} \epsilon_0 E_3(t), \quad (92)$$

where $\frac{\partial u}{\partial x}$ corresponds to the strain x_1 , e_{31} piezoelectric stress coefficient, and $\epsilon_{33}^{x_1}$ is the longitudinally clamped permittivity.

- For the electrical boundary condition of zero electric potential case (short-circuit), the external field is equal to zero. Therefore, $D_3(t) = e_{31} \frac{\partial u}{\partial x}$, and $\dot{D}_3 = e_{31} \frac{\partial^2 u}{\partial x \partial t}$. Now, the current can be written as

$$i(t) = \int_{A_e} \dot{D}_3 dA_e = w \int_{-L/2}^{L/2} \dot{D}_3 dx, \text{ and } i_0 = 2e_{31} u_0 w \omega_A = 2e_{31} w v_0. \quad (93)$$

The last transformation uses vibration velocity v_0 at the plate edge ($x = \pm L/2$), given $\omega u_0 = v_0$ for sinusoidal time varying displacement. Thus, the “force factor” (A_{31}), defined as the ratio between short circuit current and edge vibration velocity can then be written as

$$A_{31} = \frac{i_0}{v_0} = 2e_{31} w = 2w \frac{d_{31}}{s_{11}^E}. \quad (94)$$

- For open-circuit conditions, $D_3 = 0$, so the constitutive equation described in Eq. (92) is written as

$$E_3(x, t) = -\frac{e_{31}}{\epsilon_{33}^{x_1} \epsilon_0} \frac{\partial u}{\partial x}. \quad (95)$$

Assuming the variation of strain in thickness is negligible, the electric field across the thickness is uniform. Therefore, the voltage ($-V(t)/b$) should be expressed by the average of $E_3(x, t)$ in terms of x . Integrating across the length of the piezoelectric plate:

$$\int_{-L/2}^{L/2} E_3(x, t) dx = -\int_{-L/2}^{L/2} V(t)/b dx = \frac{e_{31}}{\epsilon_{33}^{x_1} \epsilon_0} \int_{-L/2}^{L/2} \frac{\partial u}{\partial x} dx,$$

We obtain the following equation, assuming free natural vibration at the antiresonance frequency in open circuit conditions:

$$\frac{LV_0}{b} = \frac{e_{31}}{\epsilon_{33}^{x_1} \epsilon_0} 2u_0, \text{ and } V_0 = \frac{2be_{31}}{L\epsilon_{33}^{x_1} \epsilon_0} u_0.$$

Thus, the “voltage factor” (B_{31}), the ratio between open circuit voltage and displacement, is expressed as

$$B_{31} = \frac{V_0}{u_0} = \frac{2b}{L} \frac{e_{31}}{\epsilon_{33}^{x_1} \epsilon_0} = \frac{2b}{L} \frac{g_{31}}{s_{11}^D} = \frac{2b}{L} h_{31}. \quad (96)$$

By applying the burst mode at resonance (short-circuit) or antiresonance (open-circuit) conditions, the force factor (A_{31}) or the voltage factor (B_{31}) can directly be obtained from the ratio between short-circuit current and edge vibration velocity, or from the ratio between open-circuit voltage and displacement. The mechanical quality factors (or elastic loss factors) and the real properties of the material can also be measured. For a damped linear system oscillating at its natural frequency, the quality factor can be described using the relative rate of decay of vibration velocity (or displacement). In general

$$Q = \frac{2\pi f}{2 \ln \left(\frac{v_1}{v_2} \right) / (t_2 - t_1)} \quad (97)$$

This equation is valid for both resonance and antiresonance modes. At resonance, the current is proportional to the vibration velocity, therefore its decay can be used. Similarly, the voltage decay can be used at antiresonance to determine the quality factor at antiresonance, which is supported by the above formula derivation.

The first resonance frequency in the k_{31} resonator corresponds to the s_{11}^E according to the equation

$$s_{11}^E = \frac{1}{(2L/f_A)^2 \rho}. \quad (98)$$

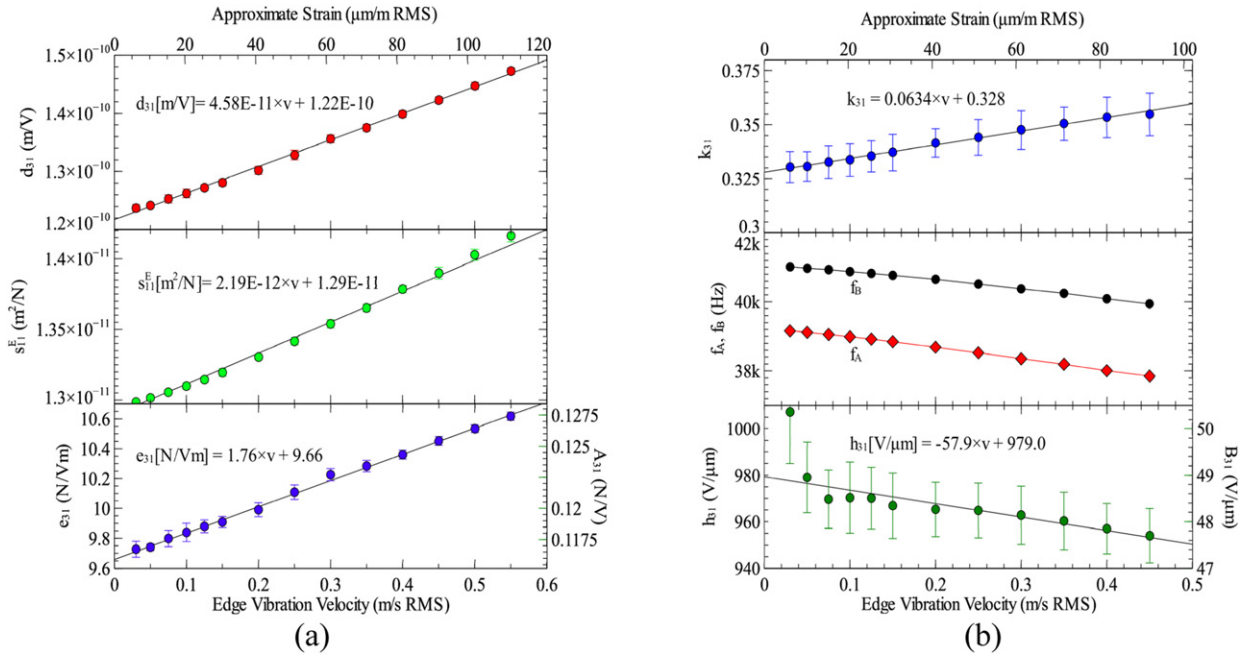


Fig. 22 (a) Resonance characterization (force factor) of soft PZT, PIC 184 k_{31} and (b) antiresonance analysis (voltage factor) and electromechanical coupling factor.

By utilizing the measurement of the force factor, the piezoelectric charge coefficient d_{31} is computed as

$$d_{31} = \frac{A_{31}s_{11}^E}{2w}. \quad (99)$$

A more common approach to calculate this coefficient, frequently used in electrical resonance spectroscopy, is as follows: The off-resonance permittivity and resonance elastic compliance can be used to separate the piezoelectric charge coefficient from the coupling coefficient measured from the relative frequency difference between resonance and antiresonance $\left[\frac{k_{31}^2}{1-k_{31}^2} = -\frac{\pi \omega_A}{2 \omega_R} / \tan\left(\frac{\pi \omega_A}{2 \omega_R}\right) \right]$, which can be expressed mathematically as follows:

$$d_{31} = k_{31} \sqrt{s_{11}^E e_{33}^X}. \quad (100)$$

However, this approach assumes that the e_{33}^X does not change in resonance conditions [off-resonance $\sim 1\text{kHz}$, resonance $\sim 40\text{kHz}$]. The calculation of d_{31} using the force factor Eq. (99) does not make this assumption, so it is expected to be more accurate.

By using piezoelectric stress coefficient (e_{31}) calculated at resonance (from the force factor) and the converse piezoelectric constant (h_{31}) calculated at antiresonance, the longitudinally-clamped permittivity e_{33}^X can be calculated in resonance/ antiresonance conditions directly. Then, e_{33}^X can be calculated using the k_{31}^2 . Permittivity has never been calculated directly in resonance conditions according to the author's knowledge. Takahashi *et al.* (1999) has reported permittivity in resonance conditions, but assumes that only the motional capacitance changes and the clamped capacitance in resonance does not change.

$$\varepsilon_0 e_{33}^X (1 - k_{31}^2) = \varepsilon_0 e_{33}^X = \frac{e_{31}}{h_{31}} = \frac{A_{31}}{B_{31}} \frac{b}{Lw} \quad (101)$$

The experimental results are shown in Figs. 22 and 23 (Shekhani *et al.*, 2016). After short-circuiting, according to the vibration velocity decay (every several-vibration cycle), we calculated necessary parameters through the force factor and voltage factor. It is notable that the one measurement takes less than 1 s (very quick!). Even if we accumulate multiple measurements for obtaining more accurate results, the total data collection time is less than 10 s, including the parameter calculation period. Regarding resonance characterization, the current and vibration data were used to calculate the force factor and the piezoelectric stress constant. Using the resonance frequency, the compliance was calculated, and hence the piezoelectric charge coefficient could be calculated as well. The resonance characterization for Soft PZT, PIC 184 is shown in Fig. 22(a), where the coefficients (e_{31} , s_{11}^E , d_{31}) increase linearly with vibration velocity. By utilizing the displacement and open circuit voltage at antiresonance, the voltage factor (B_{31}) and the converse piezoelectric coefficient (h_{31}) were calculated (see Fig. 22(b)). The coupling factor k_{31} can also be calculated using the relative difference between the resonance and antiresonance frequencies. The coupling factor increases with the vibration velocity; h_{31} decreases with increasing vibration velocity, contrary to the behavior of the other properties. That being said, it has a much smaller dependence on vibration velocity than the other properties, namely those determined at resonance.

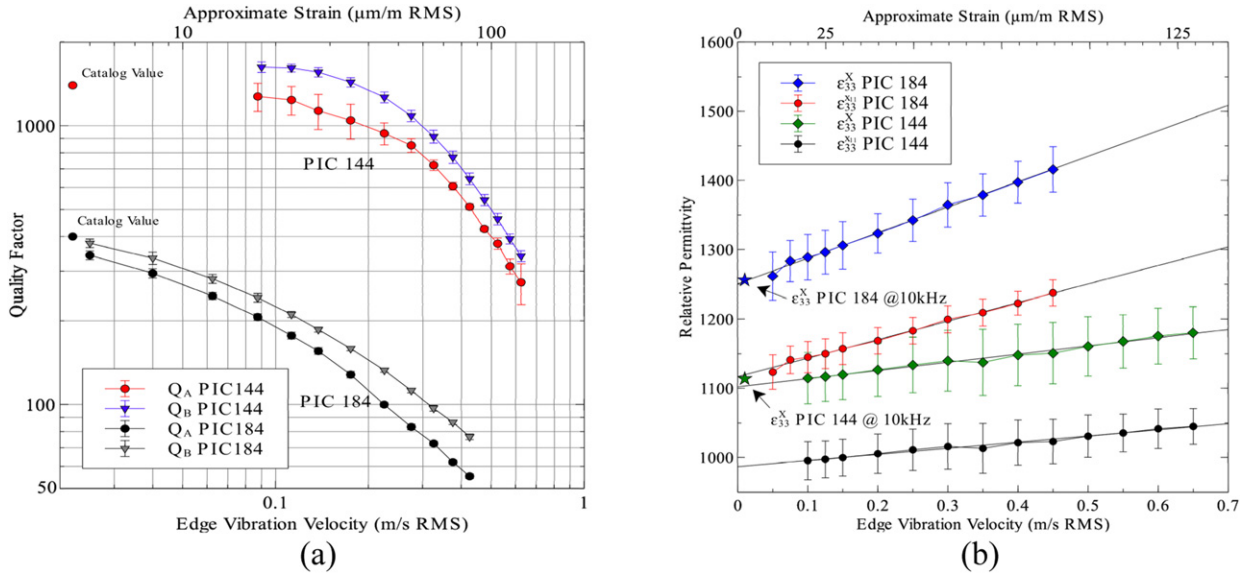


Fig. 23 (a) Change in quality factors and (b) change in dielectric permittivity with vibration velocity for PIC 144 (Hard PZT) and PIC 184 (Soft PZT).

Using the decay of vibration at resonance and antiresonance, the quality factors were calculated. Each data point used amplitude data from two vibration measurements, therefore the scale was readjusted as an average of the vibration velocity. **Fig. 23** (a) shows the results; a log-log plot was used in able to more easily distinguish and compare the trends between the two compositions. PIC 144 (Hard PZT) shows stable characteristics of the quality factor, until about vibration velocity 150 mm/s rms, after which a sharp degradation in the quality factors occurred. PIC 184 (Soft), however, showed an immediate decrease in its quality factors. Note also that Q_B is always larger than Q_A for the both materials.

Traditional methods cannot measure permittivity under resonance conditions. This is because the large vibration does not allow the dielectric response to exhibit a unique and distinct feature which can be characterized in order to compute the permittivity. This is also true for the dielectric loss. Therefore, researchers have used one of the two approaches to estimate the permittivity in high-power conditions. The first approach is to assume the permittivity measured at off-resonance applies to resonance conditions. This approach is problematic because the stress conditions and the frequency is different at resonance and therefore the property is expected to change, similar to other properties. The other approach is to assume a perturbation of the off-resonance frequency using the variation in the motional capacitance, which is proportional to d_{31}^2/s_{11}^E .

Using the force factor and the voltage factor, the permittivity under constant strain ϵ_{33}^X can be calculated directly [Eq. (101)]. Using the coupling factor k_{31} , ϵ_{33}^X can be calculated. The permittivity versus vibration velocity can be seen in **Fig. 23**(b). The off-resonance permittivity measured for the samples is in good agreement with the low vibration velocity permittivity measured through the burst technique. The off-resonance permittivity is represented as a star symbol *. The clamped and free permittivity are both changing with increasing vibration velocity. The permittivity of PIC 184 is larger than that of PIC 144, and this is expected because PIC 184 is a “soft” PZT with larger off-resonance permittivity. From the low vibration state to the high one, the permittivity of both compositions increases. However, the increase in PIC 184 is larger, demonstrating that its properties have a larger dependence on vibration conditions. Unlike an expectation, the result shown in this study demonstrates that majority of the change seen in the free permittivity can actually be attributed to the clamped permittivity change.

We improved the methodology further recently to measure the dielectric loss, in addition to the permittivity, of a piezoelectric at the resonance frequency range based on the burst excitation method (Daneshpajoooh *et al.*, 2018). Using a k_{31} type soft PZT rectangular specimen, Daneshpajoooh *et al.* investigated the “force and voltage factors” A_{31} and B_{31} under the short- and open-circuit conditions of the burst method, by focusing on their phase lags. The force factor (A_{31}) and voltage factor (B_{31}) are described as follows including the loss factors:

$$A_{31} = \frac{i_0}{v_0} = 2b \frac{d_{31}^*}{s_{11}^E} = 2w \frac{d_{31}}{s_{11}^E} \left(1 + j(\tan\phi'_{11} - \tan\theta'_{31}) \right) \quad (102)$$

$$B_{31} = \frac{V_0}{u_0} = \frac{2b}{L} \frac{d_{31}^*}{s_{11}^E \epsilon_{33}^X \epsilon_0} = \frac{2b}{L} \frac{d_{31}}{s_{11}^E \epsilon_0 \epsilon_{33}^X} \left(1 + j(\tan\phi'_{11} + \tan\delta'''_{33} - \tan\theta'_{31}) \right) \quad (103)$$

The triple prime dielectric loss $\tan\delta'''_{33}$ is close to extensive non-prime $\tan\delta_{33}$, but slightly different because the clamping is only length 1D. The permittivity and dielectric loss can be expressed:

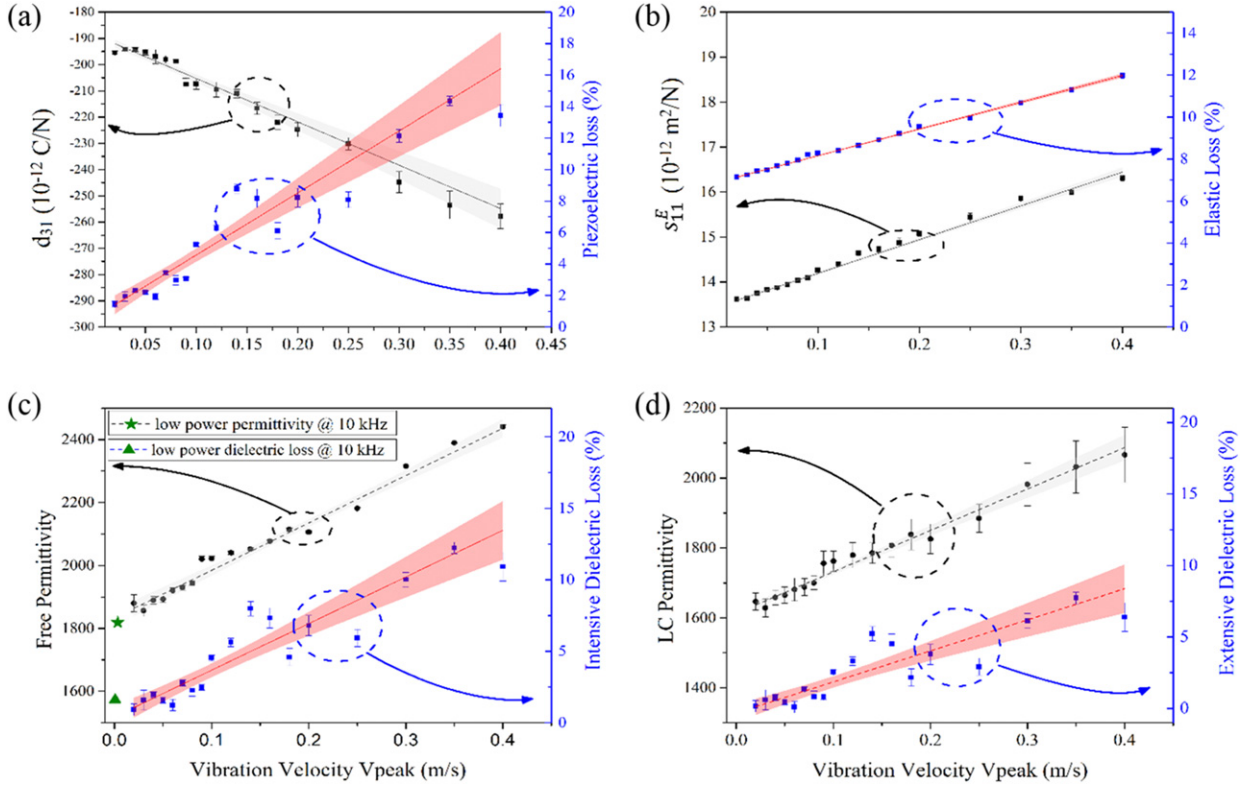


Fig. 24 Vibration level dependence of (a) piezoelectric constant (d_{31}) and piezoelectric loss ($\tan\delta_{31}$), (b) elastic compliance (s_{11}^E) and elastic loss ($\tan\phi_{11}$), and (c-d) free/clamped dielectric constants ($\epsilon_{33}^E, \epsilon_{33}^{LC}$) and corresponding dielectric losses ($\tan\delta_{33}^m, \tan\delta_{33}^e$).

$$\begin{cases} \epsilon_0 \epsilon_{33}^X (1 - k^2) = \epsilon_0 \epsilon_{33}^{X1} = \text{Re} \left\{ \frac{A_{31}}{B_{31}} \right\} \frac{b}{wL} \\ \tan\delta_{33}^m = \text{Im} \left\{ \frac{A_{31}}{B_{31}} \right\} \frac{wL}{b} \epsilon_0 \epsilon_{33}^{X1} \end{cases} \quad (104)$$

By measuring the phase lag of current over vibration velocity, and the phase lag of voltage over vibration displacement, we can obtain material properties, including loss parameters, in particular, dielectric properties at the resonance/antiresonance frequency range. **Fig. 24** shows the vibration velocity dependence of three loss factors; (a) piezoelectric constant (d_{31}) and piezoelectric loss ($\tan\delta_{31}$), (b) elastic compliance (s_{11}^E) and elastic loss ($\tan\phi_{11}$), (c), (d) free/clamped dielectric constants ($\epsilon_{33}^E, \epsilon_{33}^{LC}$) and intensive/extensive-like dielectric losses ($\tan\delta_{33}^m, \tan\delta_{33}^e$), respectively (Daneshpajooch *et al.*, 2018). All piezoelectric, elastic and dielectric losses increase with vibration velocity, as well as $d_{31}, s_{11}^E, \epsilon_{33}^X$ and ϵ_{33}^{LC} do. Note again that even the clamped permittivity and extensive-like dielectric loss change significantly with the vibration velocity!.

Loss Mechanisms in Piezoelectrics

So far, we stick on the phenomenological discussions of losses. In this section, we consider microscopic or crystallographic origins of loss mechanisms in piezoelectrics from the materials science viewpoint. Losses are considered to consist of four portions: (1) domain wall motion, (2) fundamental lattice portion, which should also occur in domain-free monocrystals, (3) microstructure portion, which occurs typically in polycrystalline samples, and (4) conductivity portion in highly-ohmic samples. However, in a typical piezoelectric ceramic case, the loss due to the “domain wall motion” exceeds the other three contributions.

Microscopic Origins of Intensive/Extensive Losses

We have discussed so far the macroscopic phenomenology of losses in piezoelectrics. We discuss here the relationship of the loss phenomenology with the microscopic origins. To make the situation simplest, we consider here only the “domain wall motion”-related losses. Taking into account the fact that the polarization change is primarily attributed to “180° domain wall” motion, while the strain is attributed to 90° (or non-180°) domain wall motion (e.g., tetragonal perovskite), we suppose that the extensive dielectric and mechanical losses are originated from 180° and 90° domain wall motions, respectively, as illustrated in **Fig. 25**. The

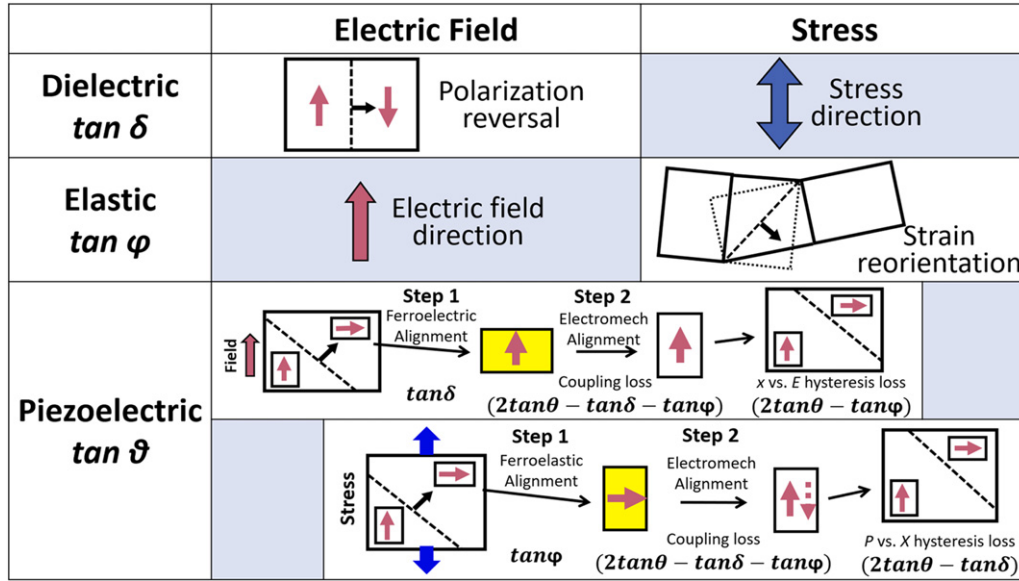


Fig. 25 Polarization reversal/reorientation model for explaining “extensive” dielectric, elastic and piezoelectric losses.

dielectric loss comes from the hysteresis during the 180° polarization reversal under E . The time delay of $\tan\delta'$ is anticipated for a specimen under pseudo-static free condition; while $\tan\delta$ under clamped condition (“damped capacitance” at the resonance frequency) [top row of Fig. 25]. Because no significant elastic energy is associated with this polarization reversal, relatively low domain wall energy is anticipated. On the contrary, the elastic loss comes from the hysteresis during the 90° polarization reorientation under X [second row of Fig. 25]. Because wide domain wall thickness is required for relaxing the significant elastic energy due to the unit cell parameter mismatch, slower domain wall speed is anticipated. The time delay of $\tan\phi'$ is anticipated for a specimen under pseudo-static short-circuit condition; while $\tan\phi$ for the resonating open-circuit condition. Regarding the piezoelectric loss, we will consider two ways: direct and converse piezoelectric effects. First, as we discussed in Section “Piezoelectric Constitutive Equations”, the reader is reminded that the piezoelectric loss is a sort of “hidden loss”, which cannot be separately observed. When we consider the direct effect [bottom row of Fig. 25] for instance, we presume that 90° domain wall motion includes two steps; Step 1: under the external tensile stress, “ferroelastic alignment” occurs; that is, the horizontally elongated cells in the upper domain will transform into vertically elongated cells, so that the 90° domain wall will move upper-rightward with time delay by $\tan\phi'$. Step 2: according to the lattice cell tetragonal shape alignment, the polarization reorientation follows, which is called “electromechanical coupling alignment”; that is, input mechanical energy is converted to electrical energy by the rate of electromechanical coupling factor square ($k^2 = d^2 / \epsilon^S \epsilon_0 \epsilon^X$) with the time delay by $(2\tan\theta' - \tan\delta' - \tan\phi')$. Note that there are two possibilities of the polarization reorientations; upward or downward. Only the “upward” selection is originated from “Gauss Law”, $\text{div}(D) = \sigma$ (charge).

Without having migrating charges σ in this crystal (i.e., highly resistive specimen), $\text{div}(D) = 0$, leading to the polarization alignment “head-to-tail” on the domain boundary, rather than “head-to-head” or “tail-to-tail”. After the “ferroelastic” transformation, this polarization alignment will need an additional time lag, which we define the “electromechanical coupling loss” including the piezoelectric loss. Superposing the “ferroelastic domain alignment” and “polarization alignment” (via Gauss Law) can generate actual charge under stress application. Adding the losses in Steps 1 and 2, we obtain the loss factor $(2\tan\theta' - \tan\delta')$ which is exactly the same as Eq. (9b). In this model, the intensive piezoelectric loss is explained as a hybrid (“hidden”) loss by superposing the 90° “ferroelastic reorientation” under X and the 90° polarization reorientation due to the “electromechanical coupling”. This is the primary reason why we cannot measure the piezoelectric loss independent from the elastic or dielectric losses experimentally.

Uchida-Ikeda Domain Reversal/Reorientation Model

We introduce the famous “Uchida-Ikeda domain reversal/reorientation model (Uchida *et al.*, 1967). During their intensive researches on polarization $P - E$ and strain $x - E$ relations, they found that the $x - P$ exhibits significant hysteresis in particular compositions of tetragonal PZTs, as shown in Fig. 26(a) (Schmidt, 1981), though the electrostrictive coupling indicates a quadratic curve, $x = QP^2$. This “clockwise hysteresis” suggests that polarization reversal seems to be delayed in comparison with the strain change. Using the polarization P and the field-induced strain x as a function of the electric field E , it is possible to estimate the volume in which 180° reversal or 90° rotation occurs. This is because the 180° domain reversal does not contribute to the induced strain, only the 90° rotation does, whereas the 180° domain reversal contributes mainly to the polarization (Fig. 26(b)). Fig. 26(c) shows the curves representing the volume fraction of 180° domains that have undergone reversal and 90° domains that have

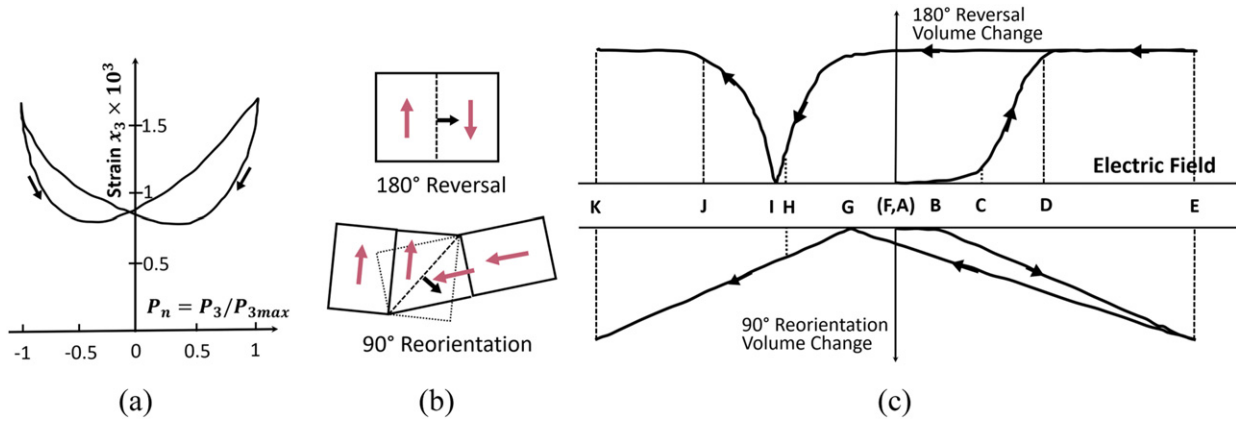


Fig. 26 (a) $x_3 - P_3$ relation in a tetragonal PLZT (6.25/50/50) ceramic at room temperature. (b) Schematic illustrations of 180° domain wall reversal and 90° domain wall reorientation. (c) Electric field dependence of the volume fraction of domains: (Top) 180° reversal and (Bottom) 90° reorientation. Notice the non-coincidence of the zero fraction points I and G (coercive field), which correspond to the 180° and 90° cases, respectively. Reproduced from Schmidt, N.A., 1981. *Ferroelectrics* 31, 105. Uchida, N., Ikeda, T., 1965. *Jpn. J. Appl. Phys.* 4, 867.

rotated by 90° as a function of applied electric field. We see from these curves that the 180° reversal occurs quite rapidly above a certain field (H) as compared to the slower process of 90° rotation started from a low field (G) (Uchida *et al.*, 1965). It is notable that at G on the curve there remains some polarization and the induced strain is zero, while at H the strain is not at a minimum, but contributions to the polarization from the 180° and 90° reorientations cancel each other so that the net polarization becomes zero. Due to a sudden change in the 180° reversal above a certain field (H), we can expect a sudden increase in the polarization hysteresis and in the dielectric loss. On the contrary, since the slope of 90° reorientation is gradual with almost constant slope, we can expect an insensitive “extensive elastic loss” with changing the external parameter, E or X , which was described in Section “Loss Measuring Technique I – Pseudo-Static Method”. This model explains the mechanical quality factor Q_m change with vibration velocity, based on the formula $Q_m^{-1} = \tan\phi' = \left(\frac{1}{1-k^2}\right)[\tan\phi + k^2(\tan\delta - 2\tan\theta)]$. When the excitation level is low, since the dielectric loss $\tan\delta$ is small, merely $\tan\phi$ contributes to the Q_m , which shows almost constant or insensitive to the vibration velocity in Fig. 16. However, due to the dramatic increase in 180° domain wall motion (i.e., the extensive dielectric loss) around a critical electric field (or the maximum vibration velocity), the dielectric loss $\tan\delta$ is increased exponentially (higher than $\tan\phi$), which leads to the apparent Q_m degradation and heat generation.

Loss Anisotropy – Crystal Orientation Dependence of Losses

Loss dissipation factors for a PZT ceramic

Zhuang *et al.* determined all 20 loss dissipation factors for a PZT ceramic using the ICAT HiPoCS admittance spectrum method described in Section “Loss and mechanical quality factor in other modes” (Zhuang *et al.*, 2010). Five specimens shown in Fig. 7 were prepared and measured on the admittance/impedance spectra for determining the piezoelectric properties. Table 2 summarizes all elastic, dielectric and piezoelectric losses determined on a Soft PZT, APC 850 (APC International, State College, PA). Compared with the error range 2%–3% of the intensive loss factors, you can notice significantly large (10 times) error range of the extensive loss factors in the table, which is originated from the error propagation due to the $[K]$ matrix calculation.

Note that the following general conclusions:

- (1) The antiresonance Q_B is always larger than the resonance Q_A in PZT's: This is a significant contradiction with the IEEE Standard (ANSI/IEEE Std 176–1987, 1987) assumption, leading to the necessity of the IEEE “Standard” revision.
- (2) The intensive (prime) losses are larger than the corresponding extensive (non-prime) losses: This is understood by the boundary condition difference between “intensive” and “extensive”; that is, “Free” or “Clamped/Constrained” conditions.
- (3) The intensive piezoelectric losses are significantly larger than the intensive dielectric or elastic losses in PZTs. That is, $\tan\theta' > (\tan\delta' + \tan\phi')/2$: This is NOT true for Pb-free piezoelectrics, as discussed later.
- (4) There is apparent loss anisotropy in dielectric, elastic and piezoelectric losses, indicating the anisotropy in domain wall mobility in the crystal.

Further specific conclusions include:

- (5) $\tan\delta_{33} < \tan\delta_{11}$: Polarization seems to be more stable along the spontaneous polarization, similar to the general permittivity trend ($\epsilon_{33}^X < \epsilon_{11}^X$).
- (6) $\tan\phi_{33} < \tan\phi_{11}$: Elastic compliance also seems to be more stable along the spontaneous polarization.
- (7) $\tan\theta_{33} < \tan\theta_{31}$: Piezoelectric constant also seems to be more stable along the spontaneous polarization.

Table 2 The 20 loss factors of Soft PZT (APC 850) with experimental uncertainties

	$\tan\phi_{11}'$	$\tan\phi_{12}'$	$\tan\phi_{13}'$	$\tan\phi_{33}'$	$\tan\phi_{55}'$	
Mean	0.01096	0.0095	0.01507	0.01325	0.0233	
Uncertainty	0.00007	0.0003	0.00034	0.00033	0.0022	
Relative	0.6%	3.2%	2.2%	2.5%	9.6%	
	$\tan\phi_{11}$	$\tan\phi_{12}$	$\tan\phi_{13}$	$\tan\phi_{33}$	$\tan\phi_{55}$	
Mean	0.0105	0.0104	0.0076	0.00433	0.0149	
Uncertainty	0.0018	0.0028	0.0013	0.00008	0.0003	
Relative	17%	28%	17%	1.7%	2.1%	
	$\tan\delta_{33}'$	$\tan\delta_{11}'$	$\tan\delta_{33}$	$\tan\delta_{11}$		
Mean	0.0143	0.0176	0.0058	0.0092		
Uncertainty	0.0002	0.0004	0.0011	0.0023		
Relative	1.4%	2.3%	20%	25%		
	$\tan\theta_{31}'$	$\tan\theta_{33}'$	$\tan\theta_{15}'$	$\tan\theta_{31}$	$\tan\theta_{33}$	$\tan\theta_{15}$
Mean	0.0184	0.0178	0.0296	0.0133	0.0004	0.0024
Uncertainty	0.0006	0.0004	0.0026	0.0081	0.0004	0.0013
Relative	3.2%	2.1%	8.8%	61%	100%	57%

Spontaneous polarization direction dependence of losses in PZT ceramics

Due to large “intensive piezoelectric loss”, the mechanical quality factor of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) ceramics at antiresonance frequency is much higher than the one at resonance frequency. Thus, driving the piezoelectric resonator at antiresonance frequency is recommended to reduce the required electric power for generating the same level of mechanical vibration. Furthermore, the maximum mechanical quality factor Q_m is realized at a driving frequency between the resonance and antiresonance frequencies basically due to a suitable compensation for the dielectric and elastic losses with the piezoelectric loss. However, since the study on piezoelectric loss has not been made intensively, its physical origin is yet unclear. Du *et al.* (1999) reported the piezoelectric “real-part” property enhancement in a polycrystalline PZT by changing polarization angle. Understanding the “imaginary-part” piezoelectric loss behavior by polarization orientation seems to be essential to clarify the origin of loss as from a domain dynamics viewpoint.

Choi *et al.* (2018) explored the loss anisotropy in piezoelectric PZT ceramics. To observe polarization angle dependence of losses, two different models for k_{31} - and k_{33} modes were prepared as shown in Fig. 27(b) and (c). The specimens were prepared with cutting and re-electroding, following the conventional ceramic processing. The polarization angle is defined by the angle of the polarization measured from the electric field direction (i.e., $0^\circ: P_S // E$; $90^\circ: P_S \perp E$) [Fig. 27(a)]. With similar elastic compliance and the same length ($L = 15$ mm), the fundamental longitudinal resonance of both models happens around 100 kHz, while the shear vibration occurs around 1 MHz.

The change of piezoelectric loss factors by polarization angle was investigated using conventional characterization method with effective k_{31} and k_{33} mode structures. 1% Nb-doped PZT ceramics (PNZT) were prepared in tetragonal (Tet), rhombohedral (Rhomb), and morphotropic phase boundary (MPB) structures with 0-, 15-, 30-, 45-, 60-, 75- and 90-degree polarization angles. Soft PZT was intentionally chosen to identify the difference the loss factor among different specimens (10 times larger than Hard PZT's). As a result, we could find out the intensive piezoelectric loss increase with the polarization angle larger than the change in intensive dielectric and elastic losses. However, serious problems were found in the k_{33} structure with small motional capacitance, which are: (1) error in 3 dB method to define mechanical quality factor due to the small damped-capacitance, (2) large relative error from indirect calculation (via $[K]$ matrix) and large impedance of k_{33} rod. Thus, we proposed a new analysis procedure to obtain the elastic parameters of k_{33} mode, using the effective k_{31} vibration mode. The sample capacitance of k_{31} mode structure, 0.24 nF, is L^2/t^2 times higher than 1.0 pF of the k_{33} mode sample, thus structural impedance problem can be minimized. Using three different effective k_{31} mode geometries with different polarization angle, we verified the IEEE Standard underestimates the elastic compliance s_{33}^E and overestimates the elastic loss $\tan\phi_{33}'$ Choi *et al.* (2017).

The crystallographic methodology to obtain all independent piezoelectric loss parameters for the polycrystalline ceramic specimen with the cant angle γ is summarized:

- (1) Off-resonance dielectric measurements

$$\varepsilon_{33,\text{eff}}^X(\gamma) = \cos^2(\gamma)\varepsilon_{33}^X + \sin^2(\gamma)\varepsilon_{11}^X$$

$$\varepsilon_{33,\text{eff}}^X(\gamma)\tan\phi_{33,\text{eff}}'(\gamma) = \cos^2(\gamma)\varepsilon_{33}^X \tan\delta_{33}' + \sin^2(\gamma)\varepsilon_{11}^X \tan\delta_{11}'$$

- (2) Effective k_{31} mode analysis

$$s_{11,\text{eff}}^E(\gamma) = \cos^4(\gamma)s_{11}^E + \sin^4(\gamma)s_{33}^E + \cos^2(\gamma)\sin^2(\gamma)[2s_{13}^E + s_{55}^E]$$

$$s_{11,\text{eff}}^E(\gamma)\tan\phi_{11,\text{eff}}'(\gamma) = \cos^4(\gamma)s_{11}^E \tan\phi_{11}' + \sin^4(\gamma)s_{33}^E \tan\phi_{33}'$$

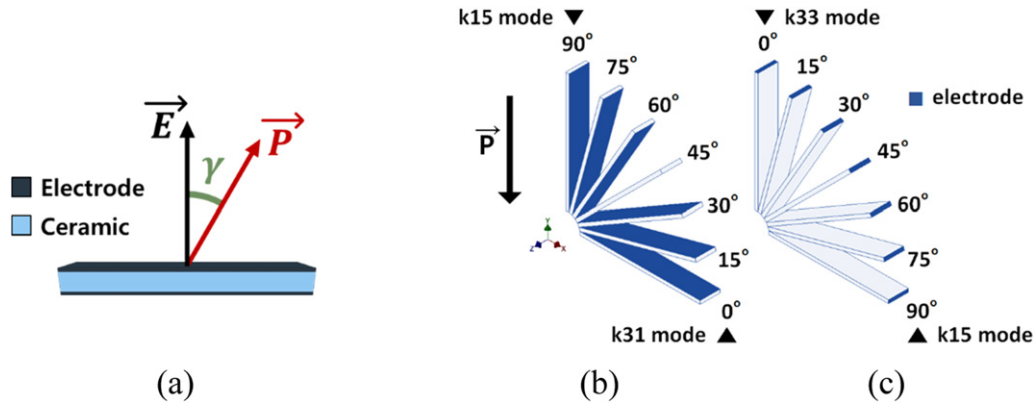


Fig. 27 Specimen configurations with various polarization directions. (a) Cant angle definition, (b) k_{31} type, (c) k_{33} -based type.

$$+\cos^2(\gamma)\sin^2(\gamma)\left[2s_{13}^E\tan\phi'_{13}+s_{55}^E\tan\phi'_{55}\right]$$

$$d_{31,eff}(\gamma)=\cos^3(\gamma)d_{31}+\cos(\gamma)\sin^2(\gamma)[d_{33}-d_{15}]$$

$$d_{31,eff}(\gamma)\tan\theta'_{31,eff}(\gamma)=\cos^3(\gamma)d_{31}\tan\theta'_{31}+\cos(\gamma)\sin^2(\gamma)\left[d_{33}\tan\theta'_{33}-d_{15}\tan\theta'_{15}\right]$$

(3) Off-resonance d_{33} measurement

$$d_{33,eff}(\gamma)=\cos^3(\gamma)d_{33}+\cos(\gamma)\sin^2(\gamma)[d_{15}+d_{31}]$$

(4) Effective k_{15} mode analysis

(a) With undistorted quadrant of Z in γ_B

$$s_{55,eff}^E(\gamma_B)=\frac{s_{55,eff}^D(\gamma_B)}{\left[1-k_{15,eff}^2(\gamma_B)\right]}=\sin^2(2\gamma_B)(s_{11}^E+s_{33}^E-2s_{13}^E)+\cos^2(2\gamma_B)s_{55}^E$$

(b) With undistorted quadrant of Y in γ_A $\tan\phi'_{13}$, $\tan\phi'_{55}$, $\tan\theta'_{33}$, $\tan\theta'_{15}$ can be calculated since

$$Q_{B,eff}(\gamma_B)=f\left\{\gamma_B,\tan\phi'_{13},\tan\phi'_{55},\tan\theta'_{33},\tan\theta'_{15}\right\}$$

$$Q_{A,eff}(\gamma_A)=f\left\{\gamma_A,\tan\phi'_{13},\tan\phi'_{55},\tan\theta'_{33},\tan\theta'_{15}\right\}$$

$$\frac{1-k_{15,eff}^2(\gamma_B)}{k_{15,eff}^2(\gamma_B)}\cdot\frac{1}{Q_{B,eff}(\gamma_B)}=\tan\delta'_{11,eff}(\gamma_B)-2\tan\theta'_{15,eff}(\gamma_B)+\frac{\tan\phi'_{55,eff}(\gamma_B)}{k_{15,eff}^2(\gamma_B)}$$

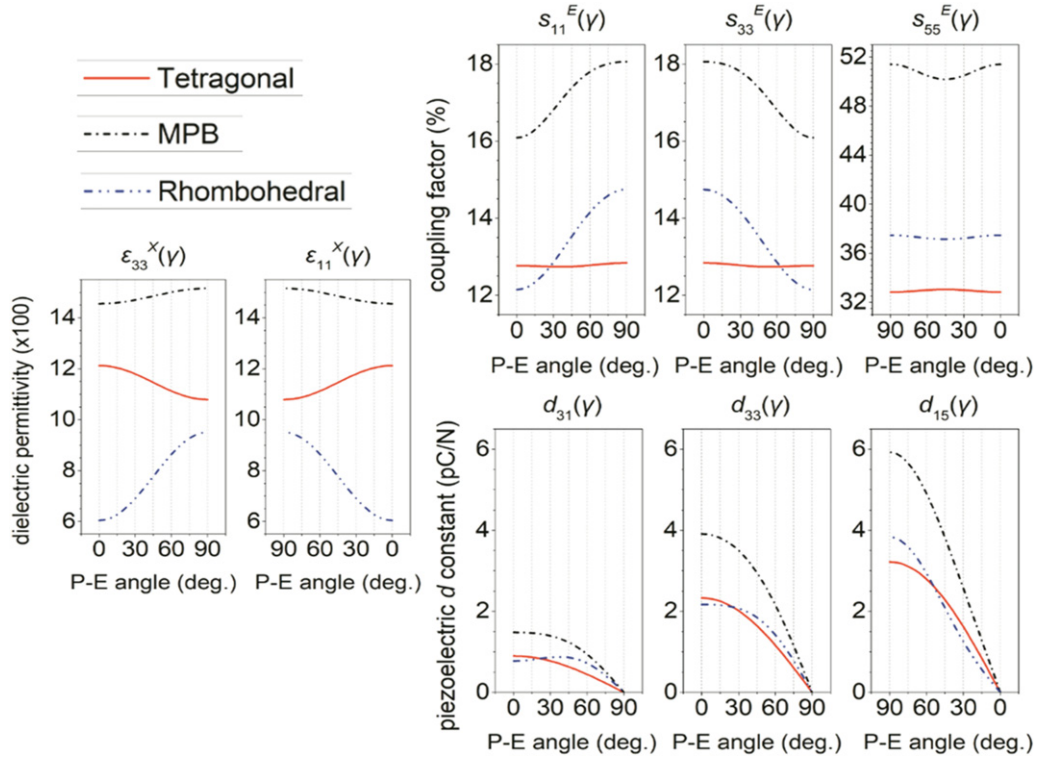
Note the shear mode parameters could only be selectively obtained due to the spurious modes. The obtained independent parameters are shown in **Table 3**.

Figs. 28 and **29** show the P - E angle dependence of effective dielectric permittivities, elastic compliances and piezoelectric constants and their corresponding intensive loss factors for Tet, MPB and Rhomb specimens. In our previous paper (Du *et al.*, 1999), we reported effective d_{33} constant enhancement in a rhombohedral soft PZT composition around 45° cut angle. However, interestingly we did not observe the peak in d_{33} value in this composition, but in d_{31} in Rhomb composition (Choi *et al.*, 2018). In order to obtain the peak in the effective piezoelectric constant d at a cant angle, significantly large d_{15} seems to be essential. Since the d_{15} is not significantly large in this composition, the peak in d_{33} value may not be observed. Compared to the permittivity perpendicular to the polarization, the permittivity along polarization is larger in Tet and smaller in Rhomb and MPB. The MPB structure has highest dielectric constant as expected. On the contrary, the dielectric loss is smaller along the polarization direction compared to the perpendicular direction, regardless of the structure. The elastic compliance along polarization direction is higher than the one perpendicular to the polarization especially in MPB and Rhomb structure. The intensive elastic loss could be considered as constant for the two directions regardless of the structure. It is interesting to note that the piezoelectric loss appeared to be smallest in Rhomb and largest in Tet structure in k_{33} and k_{15} vibration mode. Opposed to the modes, the piezoelectric loss appeared to be largest in Rhomb and smallest in Tet structure in k_{31} vibration. We believe the phenomena are strongly related with the anisotropic real parameters since both relative factors $(-d_{15}/d_{31})$ and $(-d_{33}/d_{31})$ are largest in Rhomb and smallest in Tet. It is also notable that when the relative factors are large, the corresponding piezoelectric loss is small.

More descriptions are provided on **Fig. 29**: The dielectric loss is smaller when the applied field is more aligned to polarization. Though the dielectric constant is high in MPB structure, the dielectric loss appeared to be smaller than Rhomb PNZT, presumably due to the coexisting Tet phase. The elastic loss for transversal and longitudinal mode shows a maximum while the loss for the

Table 3 The independent parameters obtained with proposed method

Tetragonal	ϵ_{33}^X	1213	ϵ_{11}^X	1079	s_{13}^E (um ² /N)	-3.72
	$\tan\delta'_{33}$ (%)	1.11	$\tan\delta'_{11}$ (%)	1.46	$\tan\phi'_{13}$ (%)	4.52
	s_{11}^E (um ² /N)	12.77	s_{33}^E (um ² /N)	12.84	s_{55}^E (um ² /N)	32.83
	$\tan\phi'_{11}$ (%)	0.91	$\tan\phi'_{33}$ (%)	0.90	$\tan\phi'_{55}$ (%)	1.88
	d_{31} (pC/N)	-90	d_{33} (pC/N)	233	d_{15} (pC/N)	322
MPB	$\tan\theta'_{31}$ (%)	1.51	$\tan\theta'_{33}$ (%)	3.03	$\tan\theta'_{15}$ (%)	3.10
	ϵ_{33}^X	1455	ϵ_{11}^X	1516	s_{13}^E (um ² /N)	-8.01
	$\tan\delta'_{33}$ (%)	1.48	$\tan\delta'_{11}$ (%)	1.62	$\tan\phi'_{13}$ (%)	4.40
	s_{11}^E (um ² /N)	16.09	s_{33}^E (um ² /N)	18.06	s_{55}^E (um ² /N)	51.41
	$\tan\phi'_{11}$ (%)	0.96	$\tan\phi'_{33}$ (%)	1.04	$\tan\phi'_{55}$ (%)	2.19
Rhombohedral	d_{31} (pC/N)	-148	d_{33} (pC/N)	391	d_{15} (pC/N)	593
	$\tan\theta'_{31}$ (%)	1.73	$\tan\theta'_{33}$ (%)	2.63	$\tan\theta'_{15}$ (%)	2.50
	ϵ_{33}^X	604	ϵ_{11}^X	950	s_{13}^E (um ² /N)	-5.13
	$\tan\delta'_{33}$ (%)	2.11	$\tan\delta'_{11}$ (%)	2.67	$\tan\phi'_{13}$ (%)	1.64
	s_{11}^E (um ² /N)	12.15	s_{33}^E (um ² /N)	14.75	s_{55}^E (um ² /N)	37.48
	$\tan\phi'_{11}$ (%)	0.74	$\tan\phi'_{33}$ (%)	0.89	$\tan\phi'_{55}$ (%)	1.30
	d_{31} (pC/N)	-77	d_{33} (pC/N)	217	d_{15} (pC/N)	383
	$\tan\theta'_{31}$ (%)	2.04	$\tan\theta'_{33}$ (%)	1.28	$\tan\theta'_{15}$ (%)	2.24

**Fig. 28** P-E angle dependence of effective dielectric permittivities, elastic compliances and piezoelectric constants for Tet, MPB and Rhomb specimens.

shear mode shows a minimum when the polarization angle is canted near 45-degree. The “intensive piezoelectric loss” factors exhibit a similar increasing tendency with angle, regardless of the crystal structure. Higher piezoelectric loss was observed when the polarization is canted. The change of piezoelectric loss was smallest in MPB PNZT, which is the most isotropic structure. Tet PNZT showed the largest polarization orientation dependence of the piezoelectric loss under k_{31} vibration mode, while Rhomb PNZT showed the largest piezoelectric loss for the k_{15} vibration mode. The “electromechanical coupling loss” for effective k_{31} vibration mode was additionally obtained using Eq. (105).

$$\frac{k''_{31}}{k'_{31}} = \frac{(2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11})}{2} \quad (105)$$

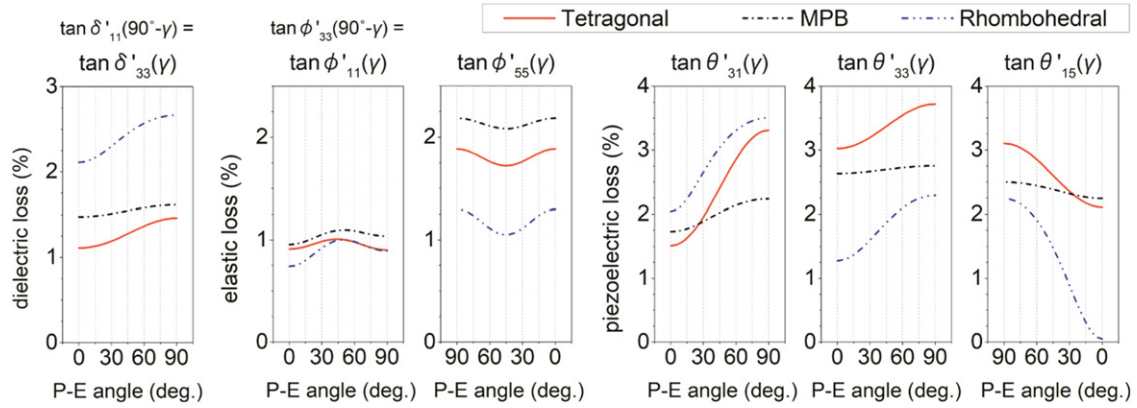


Fig. 29 Intensive loss factors versus polarization direction.

Here, k' and k'' are the real and imaginary parameters of the electromechanical coupling factor k_{31} . Note that Eq. (105) is a half of Eq. (20). The electromechanical coupling loss anisotropy in terms of crystal structures are shown in Fig. 30. The value (k''_{31}/k'_{31}) shows rather isotropic in MPB, intermediate in Rhomb, and the largest anisotropy in Tet. Under low vibration excitation, the loss factor along the spontaneous polarization direction is the smallest in Tet, followed by MPB and Rhomb. This is why most of the conventional Hard PZT composition was based on the tetragonal phase. However, under high vibration velocity level, due to large fluctuation of the P_z direction, we need to consider the loss factor effectivity at a cant angle. The reader can easily understand that the Q_M decay with vibration velocity increase will be minimized for MPB due to the isotropic loss contour. This is why the high-power density PZT composition is now based on MPB composition, not Tet or Rhomb phases. This situation will be repeated in Section "High-Power Piezoelectric Materials".

Considering 3-D clamped condition, extensive loss parameters were additionally obtained for effective k_{31} and k_{15} vibration mode using "K matrix". Fig. 31 shows the calculated "extensive loss factors". The maximum, minimum and average measured data for each geometry for effective k_{31} mode are plotted for comparison. Considering an open-circuit condition, due to the different charge development in different modes, the effective dielectric loss varies ($\tan \delta'_{11}(\gamma) \neq \tan \delta'_{33}(\frac{\pi}{2} - \gamma)$). Note that in the short-circuited condition where the charge could be well distributed, the effective dielectric loss is mode-independent ($\tan \delta'_{11}(\gamma) = \tan \delta'_{33}(\frac{\pi}{2} - \gamma)$). A similar phenomenon is observed for the elastic loss factor. The dielectric and elastic loss is mostly higher when the polarization is angled from the standard structure of each resonator, except for the shear mode in Rhomb PNZT. The piezoelectric loss is more related with the angle between the polarization and the applied electric field than dielectric or elastic loss. The piezoelectric loss is smaller when the angle is larger, meaning the compensation of dielectric and elastic loss is smaller when the polarization is canted from the applied field, from the "electromechanical coupling loss" perspective. This phenomenon could be a very important point for further study on domain dynamics. The changes are least in MPB structure which is most isotropic. In the effective k_{31} mode, the change of "extensive piezoelectric loss" is largest in Tet PNZT, which is least isotropic. In the effective k_{15} mode, the change of extensive piezoelectric loss is largest in Rhomb PNZT which has the strongest relative shear property. It is interesting to note that the "extensive piezoelectric loss" becomes "negative" in Tet PNZT when the polarization is strongly canted with respect to the applied electric field. The negative extensive piezoelectric loss in Tet structure could be obtained from both k_{31} and k_{15} vibration mode.

Unlike dielectric or elastic hysteresis, which always rotates counterclockwise for a positive compliance, the piezoelectric hysteresis could rotate counterclockwise or clockwise since the hysteresis does not have energy-density units. The counterclockwise or clockwise hysteresis corresponds to the positive or negative piezoelectric loss. A schematic illustration of the hysteresis is shown in Fig. 32.

This is the first experimental report of a "negative piezoelectric loss" at high-frequencies near resonance (~ 100 kHz for k_{31} mode and ~ 1 MHz for k_{15} mode). The issue is "the piezoelectric loss hysteresis cannot be measured separately from dielectric or elastic loss". The "electromechanical coupling factor" is responsible for the coupling loss factors and the imaginary part becomes as Eq. (106) which is equivalent to Eq. (105):

$$\frac{k''}{k'} = \frac{-2\tan\theta + \tan\delta + \tan\phi}{2} \quad (106)$$

From the equation, we can see that the piezoelectric loss compensates the elastic and dielectric loss when all parameters are positive. However, when the piezoelectric loss is "negative", the phase lag is added up, resulting in an increase of the total loss. This phenomenon could be obtained by segmenting the intensive elastic loss with extensive loss parameters as shown in Fig. 33. It is shown in most structures that the piezoelectric loss tends to compensate other losses, resulting in to lower the overall intensive elastic loss. However, in Tet PNZT with a largely canted-polarization, the piezoelectric loss adds more phase lags and increases the overall intensive elastic loss. With diminishing electromechanical coupling, the intensive and extensive elastic loss becomes the same.

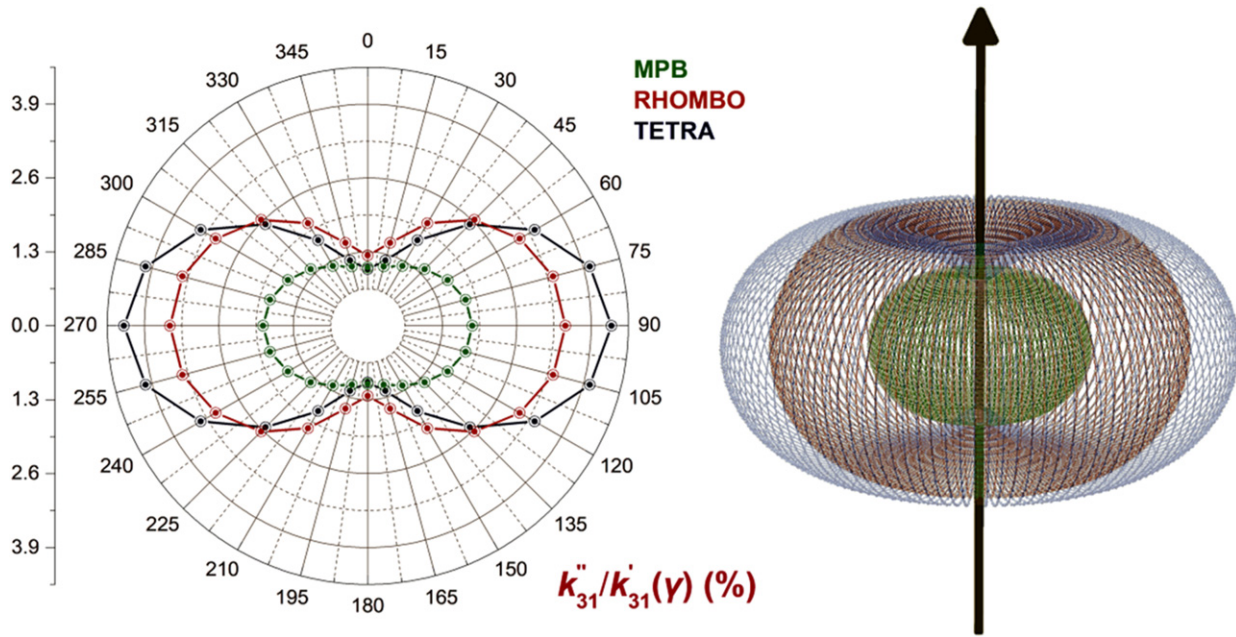


Fig. 30 Electro-mechanical coupling loss in effective k_{31} vibration mode.

A possible model of the “negative extensive loss” in tetragonal k_{31} vibration mode is proposed in Fig. 34. When the polarization canted angle γ is less than 45-degree, the positive strain will facilitate 90-degree domain wall to move leftward. Thus, a transient positive field is generated locally. Note the extensive loss parameters are considered under constant D condition which is electrically open-circuited. When the polarization canted angle is 45-degree, the positive strain will not facilitate any domain wall motion. While, when the polarization canted angle is more than 45-degree, the positive strain will facilitate 90-degree domain wall to move rightward, leading to generate transient negative electric field locally. In other words, positive and negative extensive piezoelectric loss “ $\tan\theta$ ” are anticipated for the lower and higher angled PNZT samples, as measured in the tetragonal k_{31} mode in $\tan\theta_{31}(\gamma)$ of Fig. 31 Top-Left.

Crystal orientation dependence of losses in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ single crystals

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) single crystals have been utilized in high power applications and showed significant advantages in the electromechanical coupling factor k compared with hard PZT's (Zhuang *et al.*, 2009b; Uchino *et al.*, 2011b). Recent development of the Generation III $\text{Pb}(\text{In}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PIN) -PMN-PT single crystals provides higher coercivity and Curie temperature than PMN-PT (Sun *et al.*, 2009). Piezoelectric single crystals such as PMN-PT have significant loss anisotropy and doping dependence, as shown in Fig. 35 (Zhuang *et al.*, 2009b; Rajapurkar *et al.*, 2010). Mechanical quality factors and electromechanical coupling factors for the k_{31} vibration mode under small vibration level are plotted for various orientations of single crystals in Fig. 35(a). The reader can find crystallographic orientation dependence of mechanical losses, as well as the real parameter k_{31} change: In comparison with the conventional perovskite [001] oriented specimens, the [011] plates exhibit larger k_{31} values. Fig. 35(a) shows the maximum vibration velocities (defined by 20°C temperature rise) of single crystals and PZT ceramics (k_{31} mode). The performance of single crystals is not as good as high power “hard PZT”, but better than soft PZT's. In order to improve the mechanical quality factor, Mn-doping is very effective. The maximum vibration velocity (defined by 20°C temperature rise at the node) for k_{31} -type 0.67PMN-0.33PT and 0.23PIN-0.5PMN-0.27PT specimens with different crystal orientations were measured in Fig. 35(b). Irrelevant to the composition (i.e., PIN included or not), Type B orientation ([011] plate with [100] length direction) for k_{31} vibration mode has the best high-power performance among the three. Type C orientation ([011] plate with $[0\bar{1}1]$ length direction) exhibits the second, and Type A orientation ([100] plate with [001] length direction) seems to show high losses. The ternary composition PIN-PMN-PT is better than the binary PMN-PT in terms of high mechanical quality factor, maximum vibration velocity, and low heat generation. In contrast, crystal orientation dependence of mechanical quality factor and dielectric loss of PMN-0.30PT crystals were reported by Zhang *et al.* (2009) on the k_{33} mode. In the rhombohedral PMN-PT crystals, the lowest loss factor was found along their respective polar directions, with mechanical Q_m values being > 1000 . Of particular significance is that both high electro-mechanical coupling (~ 0.9) and large mechanical $Q_m \sim 600$ were achieved in [011] poled crystals, which are consistent with our k_{31} results above.

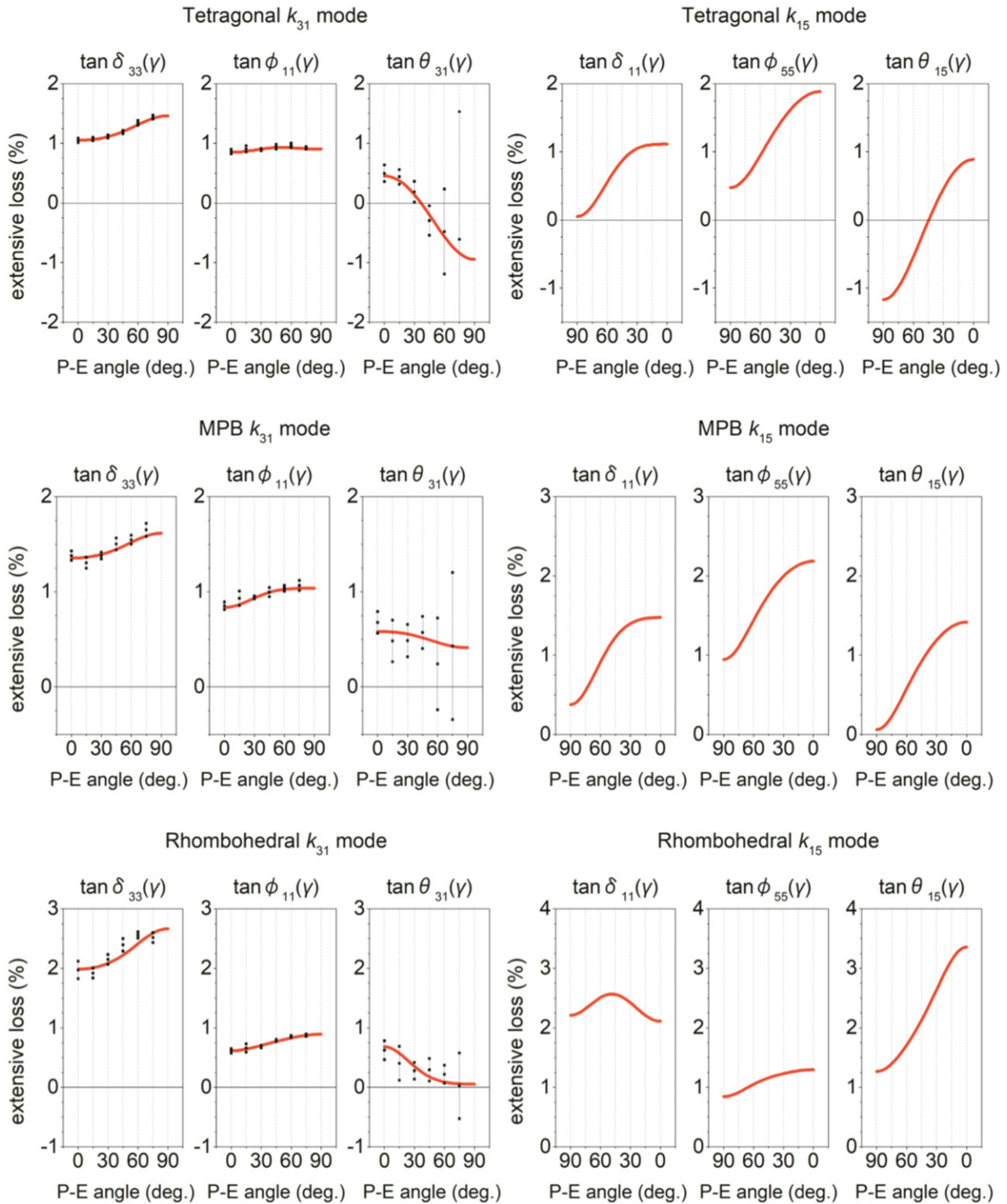


Fig. 31 Extensive loss parameters for effective k_{31} and k_{15} vibrations.

High-Power Piezoelectric Materials

Development Strategy of High-Power Piezoelectric Materials

The bottleneck of the piezoelectric devices during the miniaturization is their heat generation, associated with various losses: (1) piezoelectric material's loss, (2) multilayer structure loss (e.g., electrode loss), and (3) drive/control circuit loss. We focus on the

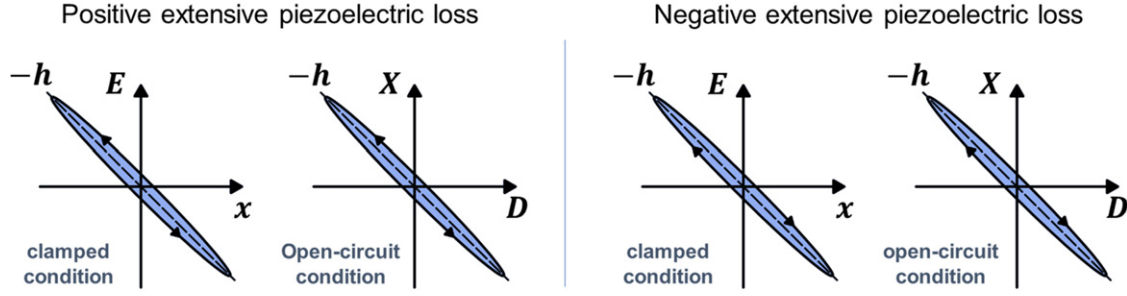


Fig. 32 Hysteresis loop for positive and negative extensive piezoelectric loss.

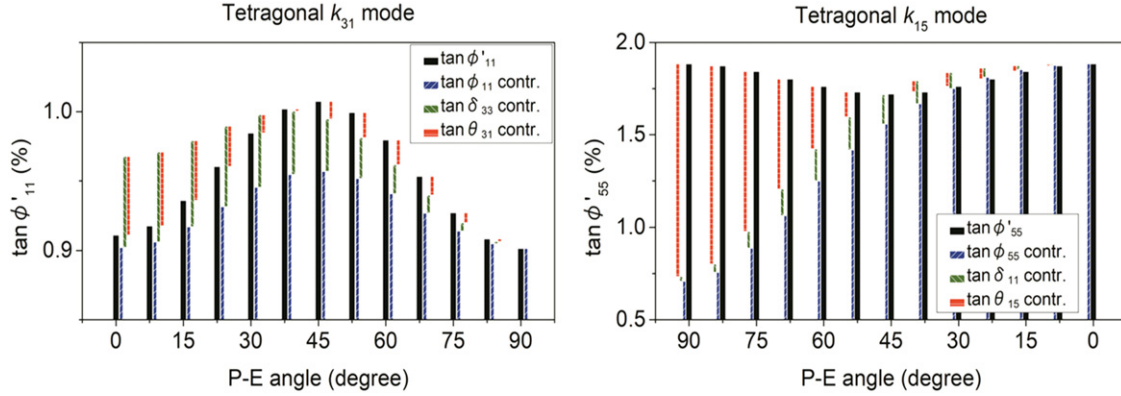


Fig. 33 Contribution of "extensive loss factors" to the "intensive elastic loss" in effective k31 and k15 vibration mode in tetragonal PNZT.

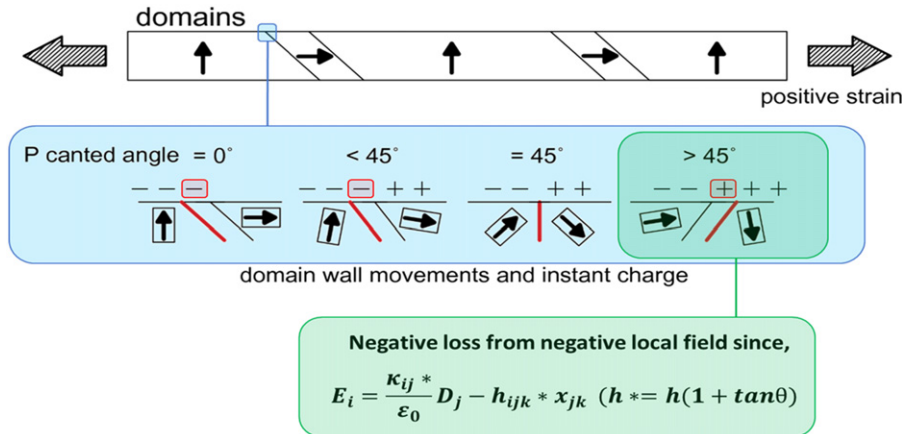


Fig. 34 A possible model of "negative" extensive piezoelectric loss in effective k₃₁ vibration mode.

material's issue in this article, remaining the others to Ref (Uchino, 2020a). Under an off-resonance (or pseudo-static) drive, the intensive dielectric loss $\tan \delta'$ is the primary loss for the heat generation [Section "Heat Generation at off-Resonance"]; while under a resonance (or antiresonance) drive, the intensive mechanical loss $\tan \phi'$ is the primary heat source [Section "Heat Generation Under Resonance Conditions"]. Recall the notion in Fig. 16, sudden decrease in the mechanical quality factor Q_m above a certain vibration velocity (i.e., "maximum vibration velocity"), which is explained by $\tan \phi' = \left(\frac{1}{1-k^2}\right)[\tan \phi + k^2(\tan \delta - 2\tan \theta)]$. We speculate the extensive mechanical loss $\tan \phi$, mainly related to the 90° (or non-180°) domain wall motion, is insensitive to the vibration velocity; while the extensive dielectric loss $\tan \delta$, related to 180° domain wall motion, increases exponentially around a certain critical vibration velocity, according to Uchida-Ikeda model introduced in Section "Loss Mechanisms in Piezoelectrics". Therefore, the development strategy of high-power piezoelectric materials should be focused on "how to decrease the 180° domain wall motion". There are four approaches: (1) ionic doping (acceptor doping creates hard PZTs), (2) material's composition (higher Curie temperature ferroelectrics exhibit higher coercive field in general), (3) Pb-free piezoelectrics (crystallographic difference and higher thermal conductivity helps higher power density), and (4) grain size control (smaller grain specimens exhibit higher maximum vibration velocity).

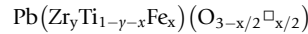
Ionic Doping – “Hard” and “Soft” PZT’s

Hard and soft PZTs

Small amounts of dopants sometimes dramatically change the dielectric and electromechanical properties of ceramics. “Donor doping” tends to facilitate domain wall motion, leading to enhanced piezoelectric charge coefficients, d , and electromechanical coupling factors, k , producing what is referred to as a “soft piezoelectric”. The soft piezoelectric materials with high piezoelectric d (lower permittivity than electrostrictive relaxor PMN-based materials) can be used for applications requiring a quick response time, such as pulse driven devices like inkjet printers. However, soft piezoelectrics generate a significant amount of heat when driven at resonance, due to their small mechanical quality factor, Q_m .

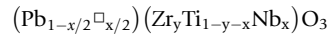
On the contrary, “acceptor doping” tends to pin domain walls and impeding their motion, leading to an enhanced mechanical quality factor, Q_m , producing what is called a “hard piezoelectric”. Hard piezoelectrics with a larger Q_m are preferred for ultrasonic transducer/motor or transformer applications, despite the slight sacrifices incurred with respect to their smaller piezoelectric strain coefficients, d , and the electromechanical coupling factors, k .

Let us consider the crystallographic defects produced on the perovskite lattice due to doping. Acceptor ions, such as Fe^{3+} , lead to the formation of oxygen deficiencies ($\square$) in the PZT perovskite lattice, and the resulting defect structure is described by:



Acceptor doping allows for the easy reorientation of deficiency-related dipoles. These dipoles are comprised of an Fe^{3+} ion (effectively the negative charge because it is situated in the $4 + \text{Ti}$ site) and an oxygen vacancy (effectively the positive charge). The oxygen deficiencies are produced at high temperature ($> 1000^\circ\text{C}$) during sintering, but the oxygen ions are still able to migrate at temperatures well below the Curie temperature (even at room temperature), because the oxygen and its associated vacancy are only $2.8 \text{ \AA}$ apart and the oxygen can readily move into the vacant site as depicted in Fig. 36(a).

In the case of donor dopant ions, such as Nb^{5+} , a Pb deficiency is produced and the resulting defect structure is designated by the following:



Donor doping is not very effective in generating movable dipoles, since the Pb ion cannot easily move to an adjacent A-site vacancy due to the proximity of the surrounding oxygen ions as depicted in Fig. 36(b). “Soft” characteristics are, therefore, observed for donor-doped materials. Another factor that should be considered here is that lead-based perovskites, such as PZT, tend to be p-type semiconductors due to the evaporation of lead during sintering and are thus already “hardened” to some extent by the lead vacancies that are produced. Hence, donor-doping will compensate the p-type, then exhibit large piezoelectric charge coefficients, d , but will also exhibit pronounced aging due to their soft characteristics.

Impurity dipole alignment models

There are three types of the impurity dipole (originated from a pair of the “acceptor ion and oxygen vacancy”) alignment possibilities as schematically visualized in Fig. 37: (1) random alignment, (2) uni-directionally fixed alignment, and (3) uni-directionally reversible alignment. Accordingly, the expected polarization versus electric hysteresis curve will be (1) higher coercive field P - E loop, in comparison with that of the original undoped ferroelectric, (2) DC bias field P - E loop, and (3) double hysteresis loop.

Dipole random alignment

The “soft” and “hard” characteristics are reflected in the coercive field E_c , or more precisely in the stability of the domain walls. A piezoelectric is practically classified as “hard” if it has a coercive field greater than 1 kV/mm , and “soft” if the coercive field is less than 100 V/mm . “Semi hard” or “semi-soft” is used for the intermediate E_c materials. Consider the transient state of a 180° domain reversal that occurs at a domain wall associated with a configuration of head-to-head polar domains in Fig. 38. Recall the Gauss’ law:

$$\text{div } D = \rho, \quad (107)$$

where D is the electric displacement and ρ is the charge density. The domain wall is very unstable in a highly insulating material ($\rho = 0$) and therefore readily reoriented and the coercive field for such a material is found to be low. However, this head-to-head configuration is stabilized in a more conductive (some movable charges) material and thus a higher coercive field is required for polarization reversal and the associated domain wall movement to occur. Fig. 38 illustrates these two cases. The free charges associated with defect structures present in a doped PZT material. The presence of acceptor dopants, such as Fe^{3+} , in the perovskite structure is found to produce oxygen deficiencies, while donor dopants, such as Nb^{5+} , produce A-site deficiencies. Only the acceptor doping generates movable dipoles, which correspond to ρ and can stabilize the domain walls.

These simple defect models help us to understand and explain various changes in the properties of a perovskite ferroelectric of this type that occur with doping. The effect of donor doping in PZT on the field-induced strain response of the material was examined for the soft piezoelectric composition $(\text{Pb}_{0.73}\text{Ba}_{0.27})(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$ (Hagimura and Uchino, 1989). The parameters maximum strain, x_{max} , and the degree of hysteresis, $\Delta x/x_{\text{max}}$, are defined in terms of the hysteresis response depicted in Fig. 39(a). The maximum strain, x_{max} , is induced under the maximum applied electric field. The degree of

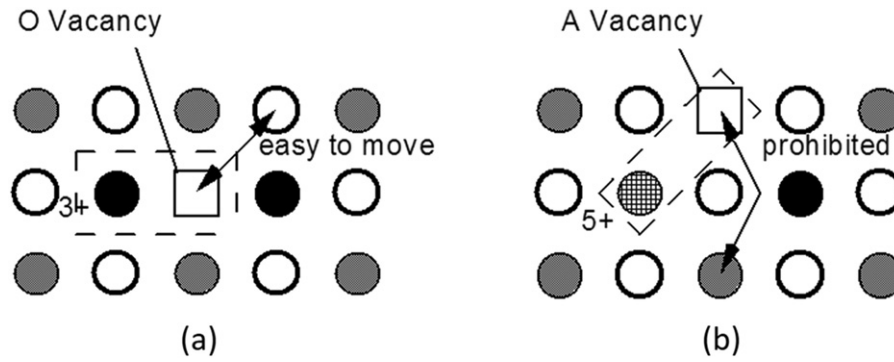


Fig. 36 Lattice vacancies in PZT containing: (a) acceptor and (b) donor dopants.

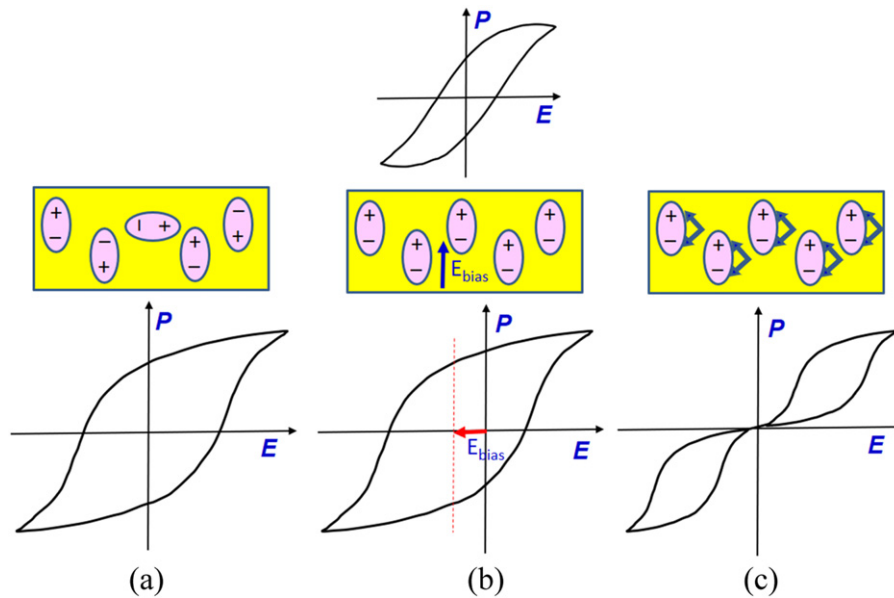


Fig. 37 Impurity dipole alignment possibility and the expected P vs. E hysteresis curves: (a) random alignment, (b) uni-directionally fixed alignment, and (c) uni-directionally reversible alignment.

hysteresis, $\Delta x/x_{max}$, is just the ratio of the strain induced by half the maximum applied electric field to the maximum strain, x_{max} . The effect of acceptor and donor dopants (2 at% concentration) on the induced strain and degree of hysteresis is shown in Fig. 39(b). It is seen that materials incorporating high valence donor-type ions on the B-site (such as Ta^{5+} , Nb^{5+} , W^{6+}) exhibit excellent characteristics as positioning actuators, namely, enhanced induced strains and reduced hysteresis. On the other hand, the low valence acceptor-type ions ($+1$, $+2$, $+3$) tend to suppress the strain and increase the hysteresis and the coercive field. Although acceptor-type dopants are not desirable when designing actuator ceramics for positioner applications, acceptor doping is important in producing “hard piezoelectric” ceramics, which are preferred for ultrasonic transducer/motor applications. In this case, the acceptor dopant acts to pin domain walls, resulting in the high mechanical quality factor characteristic of a hard piezoelectric.

Let us now consider high-power piezoelectric ceramics for ultrasonic (AC resonance drive) applications. When the ceramic is driven at a high vibration rate (that is, under a relatively large AC electric field) heat will be generated in the material resulting in significant degradation of its piezoelectric properties. A high-power device such as an ultrasonic motor therefore requires a very “hard” piezoelectric with a high mechanical quality factor, Q_m , to reduce the amount of heat generated. The temperature rise (at the nodal point, or plate center of a rectangular specimen) in undoped, Nb-doped, and Fe-doped PZT k_{31} plate specimens is plotted as a function of vibration velocity (rms value measured at the plate end) in Fig. 40(a) (Takahashi *et al.*, 1993). A significant reduction in the generation of heat is apparent for the Fe-doped (acceptor-doped) ceramic. Most commercially-available hard PZT ceramic plates tend to generate the maximum vibration velocity around 0.3 m/s (rms) when operated in a k_{31} mode. Even when operated under the higher applied electric field strengths, the vibration velocity will not increase for these devices; the additional energy is just converted into heat.

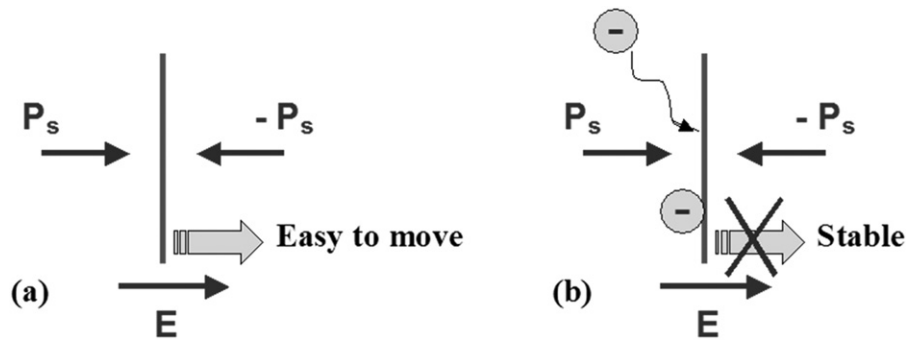


Fig. 38 Stability of 180° domain wall motion in: (a) an insulating material and (b) a material with free charges.

Unidirectionally fixed dipole alignment

Higher maximum vibration velocities have been realized in PZT-based materials modified by dopants that effectively reduce the amount of heat generated in the material and thus allow for the higher rates of vibration. NEC, Japan, developed multilayer piezoelectric transformers with the $(1 - z)\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 - z\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3$ composition (Takahashi *et al.*, 1995). The maximum vibration velocity of 0.62 m/s occurs at the $x = 0.47$, $z = 0.05$ composition and is accompanied by a 40°C temperature rise from room temperature. The incorporation of additional “rare earth dopants” to this optimum base composition results in an increase in the maximum vibration velocity to 0.9 m/s at 20°C temperature rise, already introduced in Fig. 40(b) (Ryu *et al.*, 2003; Gao *et al.*, 2002). This increased vibration rate represents a three-fold enhancement over that typically achieved by commercially produced hard PZT devices and corresponds to an increase in the vibration energy density by an order of magnitude with minimal heat generated in the device. The mechanism of this stable high power performance is explained below.

In the previous Section “Dipole random alignment”, we introduced so-called “domain wall pinning model”: acceptor ions, such as Fe^{3+} , introduce oxygen deficiencies in the PZT crystal (in the case of donor ions, such as Nb^{5+} , Pb deficiency is introduced). Thus, this easy reorientation of deficiency-related dipoles leads to “hard” characteristics. However ICAT/Penn State University explored the origin of our high-power piezoelectric ceramics, and found that the “internal bias field model” seems to be better for explaining our material’s characteristics, instead of “oxygen quick drift domain wall pinning model” (Gao and Uchino, 2004; Gao *et al.*, 2006, 2007a,b).

Gao *et al.* (2006) reported very suggestive results in the mechanical Q_m increase with “time lapse” (minute) after the electrical poling, measured for various commercial soft and hard PZTs, PSM-PZT, and PSM-PZT doped with Yb in Fig. 41(a). It is worth noting that the Q_m values for commercial hard PZT and our high power piezoelectrics were almost the same, slightly higher than soft PZTs, and around 200–300 immediately after the poling. After a couple of hours passed, the Q_m values increased more than 1000 for the “hard materials”, while no change was observed in the “soft material”. The increasing slope is the maximum for the “Yb-doped PSM-PZT”. This result shows a contradiction that the gradual increase in “a couple of hours” in the Q_m cannot be explained by the above-mentioned “domain wall pinning” model, which is hypothesized that the oxygen-deficit-related dipole should move rather quickly in milli-second scale during electric field cycle to reflect large coercive field in the P - E hysteresis.

Fig. 41(b) shows the polarization vs. electric field hysteresis curves measured for the Yb-doped $\text{Pb}(\text{Mn,Sb})\text{O}_3$ - PZT sample immediately after poling (fresh), 48 h after, and a week after (aged) (Gao *et al.*, 2006, 2007a). Remarkable aging effects could be observed: (1) in the decrease in the magnitude of the remnant polarization, and (2) in the “positive internal bias electric field” growth (i.e., the hysteresis curve shift leftwards with respect to the external electric field axis). The phenomenon (1) can be explained by the local domain wall pinning effect, but the large internal bias (close to 1 kV/mm) growth (2) seems to be the origin of the high-power characteristics. Suppose that the vertical axis in Fig. 26(c) (Uchida-Ikeda domain reorientation model) shifts rightwards (according to 1 kV/mm “positive internal bias field”), the larger negative electric field is required for realizing the 180° polarization reversal, leading to the resistance enhancement against generating the hysteresis or heat with increasing the applied AC voltage.

Gao *et al.* (2007a,b) proposed the origin of this “internal bias electric field” growth with time. Based on the presence of the oxygen deficiencies and the relatively slow (a couple of hours) growth rate, we assume here the oxygen deficiency diffusion model, which is illustrated in Fig. 42 (). Under the electrical poling process, the “defect dipole” P_{defect} (a pair of acceptor ion and oxygen deficiency) will be arranged parallel to the external electric field. After removing the field, the “oxygen diffusion” starts to occur, which can be estimated in a scale of hour at room temperature. Taking into account slightly different atomic distances between the A and B ions in the perovskite crystal in a ferroelectric (“asymmetric”) phase, the oxygen diffusion probability will be slightly higher for the downward (due to the spontaneous polarization upward), as shown in the figure schematically, leading to the increase in the defect dipole with time. This may be the origin of the “internal bias electric field”. The reader can easily understand that the dipole alignment is unidirectionally fixed along the polarization direction in this model.

Unidirectionally reversible dipole alignment

Tan and Viehland reported a double hysteresis in K-doped PZT ceramics (PKZT) (Tan and Viehland, 1997). Fig. 43(a) shows a P - E hysteresis curved observed in an “aged” sample of 4 at% K-doped $\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$. Probably due to the unidirectionally

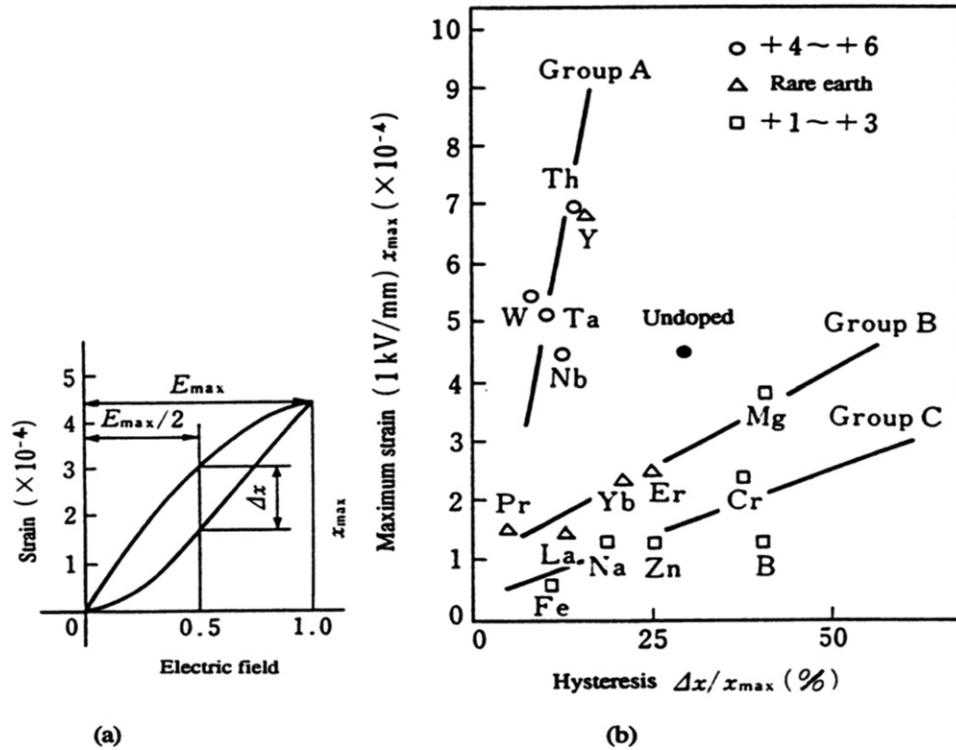


Fig. 39 Maximum strain and hysteresis in $\text{Pb}_{0.73}\text{Ba}_{0.27}(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$ -based ceramics: (a) hysteresis curve showing the parameters needed for defining the maximum strain, $x_{\max}$, and the degree of hysteresis, $\Delta x/x_{\max}$, and (b) the dopant effect on actuator parameters. Reproduced from Hagimura, A., Uchino, K., 1989. *Ferroelectrics* 93, 373.

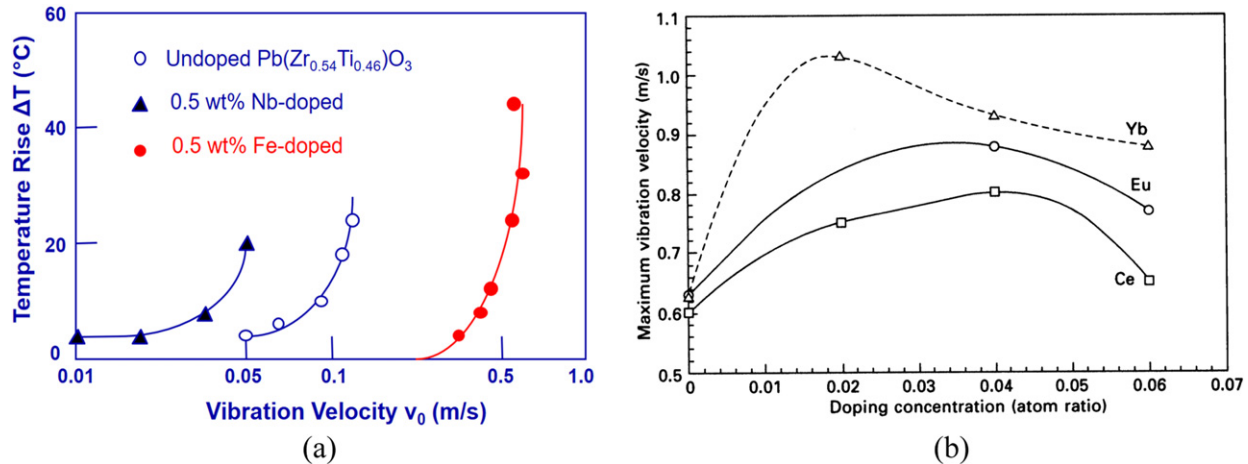


Fig. 40 (a) Temperature rise, ΔT , plotted as a function of effective vibration velocity, v_0 , for undoped, Nb-doped, and Fe-doped PZT samples. (b) Dependence of the maximum vibration velocity v_0 (20°C temperature rise) on the atomic % of rare-earth ion, Yb, Eu or Ce in the $\text{Pb}(\text{Mn,Sb})\text{O}_3$ (PMS) – PZT based ceramics. Reproduced from Takahashi, S., Hirose, S., 1993. *Jpn. J. Appl. Phys.* 32, 2422–2425. Ryu, J., Kim, H.W., Uchino, K., Lee, J., 2003. Effect of Yb addition on the sintering behavior and high power piezoelectric properties of $\text{Pb}(\text{Zr,Ti})\text{O}_3\text{-Pb}(\text{Mn,Nb})\text{O}_3$. *Jpn. J. Appl. Phys.* 42 (3), 1307–1310. Gao, Y., Uchino, K., Viehland, D., 2002. Rare earth metal doping effects on the piezoelectric and polarization properties of $\text{Pb}(\text{Zr,Ti})\text{O}_3\text{-Pb}(\text{Sb,Mn})\text{O}_3$ ceramics. *J. Appl. Phys.* 92, 2094–2099.

(along the spontaneous polarization direction) switchable impurity dipole, though the hysteresis curve is symmetry (no internal DC bias field), the polarization is pinched around $E = 0$. However, with increasing the temperature, this “pinching curve” was released to the normal high coercive field hysteresis. 150°C is reported to be the temperature near which mobile defects begin to move to be a random alignment. This unidirectionally-reversible dipole alignment will not contribute to the loss reduction nor reduction of heat generation.

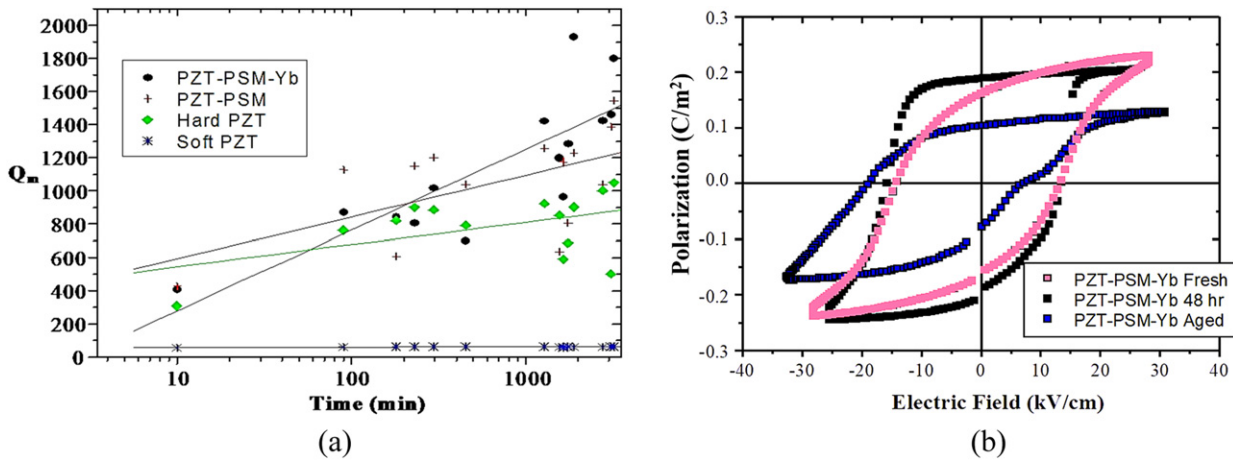


Fig. 41 (a) Change in the mechanical Q_m with time lapse (minute) just after the electric poling, measured for various commercial soft and hard PZT's, PSM-PZT, and PSM-PZT doped with Yb. (b) Polarization versus electric field hysteresis curves measured for the Yb-doped $\text{Pb}(\text{Mn,Sb})\text{O}_3$ -PZT specimen just after poling (fresh), 48 h after, and a week after (aged). Reproduced from Gao, Y., Uchino, K., Viehland, D., 2006. Time dependence of the mechanical quality factor in 'hard' lead zirconate titanate ceramics: Development of an internal dipolar field and high power origin. Jpn. J. Appl. Phys. 45 (12), 9119–9124.

Composition Dependence of Piezoelectric Losses

PZT based ceramics

"High power density" in mechanical output energy converted from the input electrical energy under the drive condition is defined from the maximum vibration velocity with 20°C temperature rise. The mechanical power density can be evaluated by the square of the "maximum vibration velocity" (v_0^2) for similar mass density piezo-ceramics, which is a sort of material's constant. Remember that there exists the "maximum mechanical energy density", above which level the piezoelectric material becomes a merely "ceramic heater". Let us discuss high vibration velocity materials based on PZT's first. Fig. 44 shows the mechanical Q_m versus basic composition x at two vibration velocities (RMS) $v_0 = 0.05$ m/s and 0.5 m/s for a so-called hard PZT, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ doped with 2.1 at% of Fe (Takahashi *et al.*, 1993, 1995). Under small vibration velocity excitation, the mechanical quality factor Q_m shows the largest in the "tetragonal phase", followed by the rhombohedral, then the lowest at the morphotropic phase boundary (MPB) composition. Therefore, commercially-available hard PZTs are mostly prepared with the tetragonal phase compositions [This was a previous big misconception!]. However, with increasing the excitation level, we are actually surprised to observe a significant decrease in the Q_m in tetragonal compositions: "the best material becomes the worst material" with an increase in vibration velocity! The decrease in mechanical Q_m with an increase of vibration level was discovered to be minimum around the MPB (52/48). In other words, the smallest Q_m material under a small vibration level becomes the highest Q_m material under a large vibration level, which is very suggestive. The reader should notice that most of the materials with $Q_m > 1200$ in a company catalog are degraded dramatically at an elevated power measurement.

The conventional commercial piezo-ceramics have the limitation in the maximum vibration velocity ($v_{\max}$) with the typical rms value of $v_{\max}$, defined by the temperature rise of 20°C from room temperature, is around 0.3 m/sec for rectangular samples operating in the k_{31} mode (like a Rosen-type transformer) which corresponds to ~ 5 W/cm³. $\text{Pb}(\text{Mn,Sb})\text{O}_3$ (PMS) - lead zirconate titanate (PZT) ceramics with the $v_{\max}$ of 0.62 m/sec are currently used for NEC transformers [~ 25 W/cm²] (Takahashi *et al.*, 1995). By doping the PMS-PZT or $\text{Pb}(\text{Mn,Nb})\text{O}_3$ -PZT with "rare-earth ions" such as Yb, Eu and Ce, we further improved high-power piezoelectrics, which can operate with $v_{\max}$ up to 1.0 m/sec (Ryu *et al.*, 2003; Gao and Uchino, 2004). Compared with commercially available piezoelectrics, 10 times higher input electrical energy and output mechanical energy can be expected from these new materials without generating significant temperature rise, which corresponds to ~ 50 W/cm³.

$\text{Pb}(\text{In}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PIN-PMN-PT)

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT) single crystals have been utilized in high-power applications and showed significant advantages in the electromechanical coupling factor k . Recently the Generation III $\text{Pb}(\text{In}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PIN)-PMN-PT single crystals were developed with a higher Curie temperature so that higher coercivity and harder characteristics are expected than PMN-PT (Sun *et al.*, 2009). Piezoelectric PIN-PMN-PT single crystals have composition dependence of performances, as shown in Fig. 35 (Zhuang *et al.*, 2009b; Rajapurkar *et al.*, 2010). Improvement in the mechanical quality factor is not clear under small excitation level in Fig. 35(a), but it is clear in the maximum vibration velocity in Fig. 35(b). The maximum vibration velocity (defined by 20°C temperature rise at the node) for k_{31} -type is definitely higher in 0.23PIN-0.5PMN-0.27PT than that in 0.67PMN-0.33PT specimens regardless of different crystal orientations.

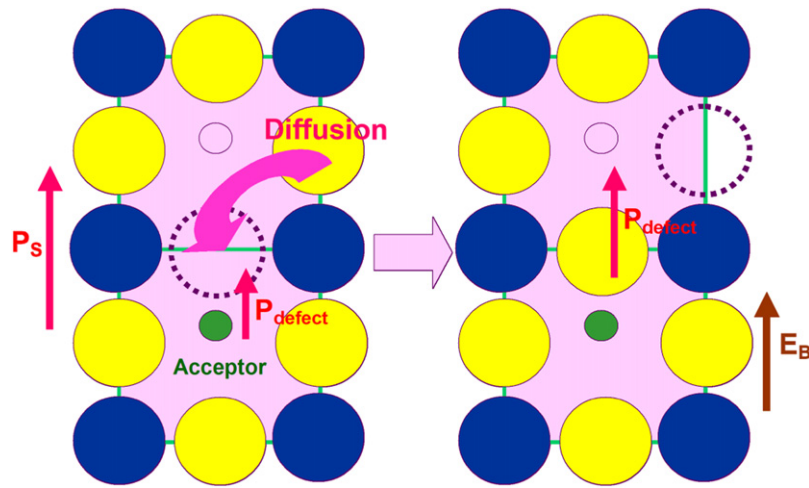


Fig. 42 Oxygen deficiency diffusion model for explaining the internal bias electric field growth. Reproduced from Gao, Y., Uchino, K., Viehland, D., 2007a. Domain wall release in ‘hard’ piezoelectrics under continuous large amplitude AC Excitation. *J. Appl. Phys.* 101 (11), 114110. Gao, Y., Uchino, K., Viehland, D., 2007b. Effects of thermal and electrical history on ‘hard’ piezoelectrics: A comparison of internal dipolar fields and external DC bias. *J. Appl. Phys.* 101 (5), 054109.

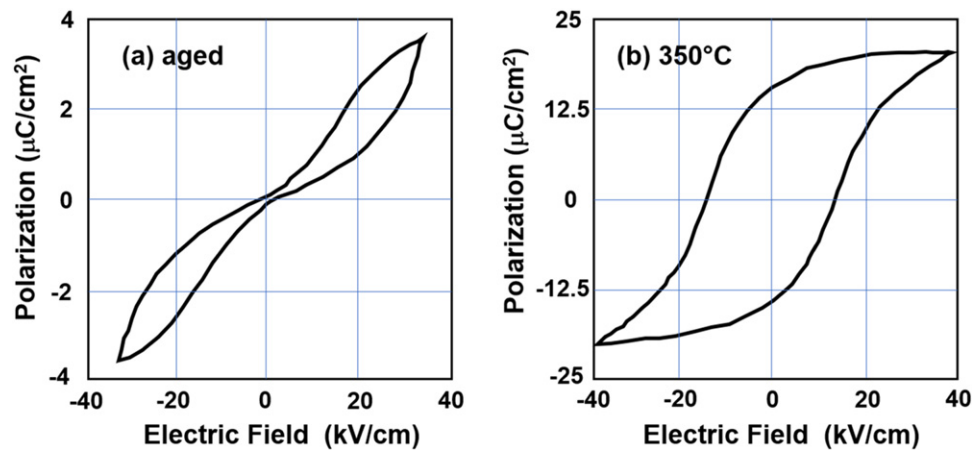


Fig. 43 (a) Room temperature P - E hysteresis curve observed in an ‘aged’ 4 at% doped $\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$. (b) The P - E hysteresis at 350°C . Reproduced from Tan, Q., Viehland, D., 1997. *Philosophical Magazine*.

Pb-Free Piezoelectrics

RoHS regulation

In 2006, European Union started RoHS (Restrictions on the use of certain Hazardous Substances), which explicitly limits the usage of lead (Pb) in electronic equipment because of its toxicity. Basically, we may need to regulate the usage of lead zirconate titanate (PZT), most widely-used piezoelectric ceramics in these 10 years. Pb (lead)-free piezoceramics have started to be developed after 1999, which are classified into three; $(\text{Bi},\text{Na})\text{TiO}_3$ (BNT) (Tou *et al.*, 2009), $(\text{Na},\text{K})\text{NbO}_3$ (NKN) (Saito *et al.*, 1996) and tungsten bronze (TB) (Doshida, 2009). NKN systems exhibit the highest performance because of the morphotropic phase boundary (MPB) usage, and in particular, in a structured ceramic manufacturing with flaky powders. TB types are another alternative choice for resonance applications, because of high Curie temperature and low loss. A sophisticated preparation technology for fabricating oriented ceramics was developed with a multilayer configuration: that is, preparation under strong magnetic field (Doshida, 2009).

Though there is a lot of research related with lead-free piezoelectric materials recently, there is limited research data on high-power characterization of the lead-free piezoelectric materials. The author’s group enlightened the high-power characteristics of Pb-free piezoelectric ceramics compared to hard PZT’s. Though the RoHS regulation is the trigger of the Pb-free piezoelectric development, we could find superior performances of Pb-free piezoelectrics to those of conventional PZT’s.

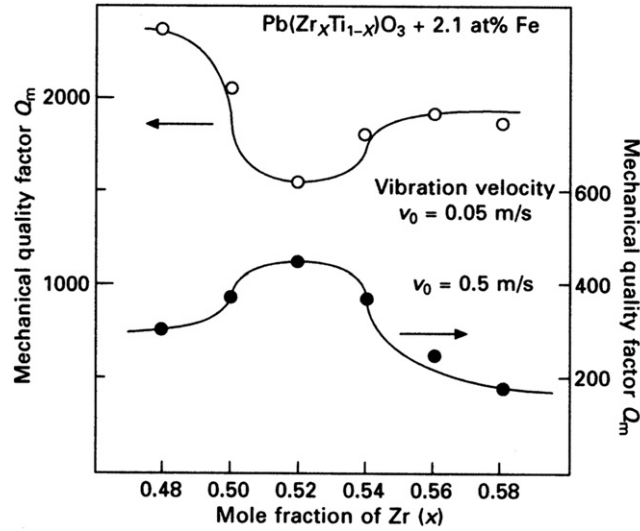


Fig. 44 Mechanical Q_m versus basic composition x at two rms vibration velocities $v_0 = 0.05$ m/s and 0.5 m/s for $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ doped with 2.1 at% of Fe.

High-power performance in Pb-free piezoelectrics

High power characteristics were investigated with the HiPoCS (Gurdal *et al.*, 2013; Hejazi *et al.*, 2014). Tested disk-shape specimens were prepared in collaboration with Toyota R&D, Honda Electronics, Korea University, and Rutgers University, including: (a) NKN - $(\text{Na}_{0.5}\text{K}_{0.5})(\text{Nb}_{0.97}\text{Sb}_{0.03})\text{O}_3$ prepared with 1.5% mol CuO addition, (b) BNT-BT-BNMN - $0.82(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - 0.15\text{BaTiO}_3 - 0.03(\text{Bi}_{0.5}\text{Na}_{0.5})(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, (c) BNKLT - $0.88(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - 0.08(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3 - 0.04(\text{Bi}_{0.5}\text{Li}_{0.5})\text{TiO}_3$ with Mn-doped and -undoped. The hardening can be achieved by doping Fe and Mn in the PZT's; while Cu in NKN, Mn in BNT based ceramics.

It is worth noting that the "maximum vibration velocity" (v_{ms}) reaches 0.8 m/s in all three Pb-free piezoceramics, but that this does not directly mean the superiority of Pb-free; a low mass density material can easily generate large vibration velocity. Therefore, in order to compare the high-power performance superiority fairly to PZT's, "mechanical energy density ($\frac{1}{2}\rho v_{ms}^2$)" should be used rather than the "maximum vibration velocity". Fig. 45 shows the high-power results for disk specimens; mechanical quality factors Q_A at resonance (a) and Q_B at antiresonance (b) are plotted as a function of "mechanical energy density". First, the mechanical quality factors Q_A and Q_B do not decrease with increasing vibration level [mechanical energy density ($\frac{1}{2}\rho v_{ms}^2$)] in Pb-free piezoelectrics, in comparison with PZT's trend. Second, the maximum mechanical energy density defined with 20°C increase of the temperature on the nodal point in NKN and BNT-BT-BNMN is superior, compared to hard-PZT's with their sharp decrease in Q_A with increasing vibration level. At antiresonance, the high-power behavior trend for this material changes similar to the resonance trend. The mechanical quality factor Q_B also remained constant up to the maximum vibration level. Regarding the Figure-Of-Merit (actual vibration level, $Q_m \cdot k_p$) change with the vibration level, the PZT shows better performance in the low power vibration range, because of higher k_p value in PZT. However, in the high-power range ($> 1000 \text{ J/m}^3$), only Pb-free piezoelectrics can practically be adopted. As mentioned in Section "Temperature distribution profile versus thermal diffusivity", much higher maximum vibration velocity in NKN ceramics (Gurdal *et al.*, 2013) is partially related with larger "thermal conductivity" in the NKN-based material [$\kappa = 3.10 \text{ (W/m K)}$] in comparison with $\kappa = 1.25$ in hard PZT: unreported data].

Third, the Q_A and Q_B values in Pb-free are almost the same up to maximum vibration velocity v_{max} , which is distinctly different from the hard-PZT, where Q_B is always greater than Q_A , experimentally (due to the significant intensive piezoelectric loss). Comparison of mechanical quality factors Q_A and Q_B provides an aspect to the material losses (i.e., dielectric ($\tan\delta'$), mechanical ($\tan\phi'$), and piezoelectric ($\tan\theta'$)) behavior for different compositions. Both soft and hard PZT's result in $Q_B > Q_A$, as we already discussed. While, regarding the Pb-free piezoelectrics, hard Bi-perovskite ceramics (i.e., BNT-BKT-BLT-Mn and BNT-BT-BNMN) seem to have the minimum influence from the piezoelectric loss ($\tan\theta'$) when excited at high vibration levels since they showed the $Q_A > Q_B$ relationship. Cu-doped NKN ceramics seem to have more influence ($Q_A \cong Q_B$ for NKN-Cu) from the piezoelectric loss ($\tan\theta'$). Softer BNT-BKT-BLT ceramics seem to have the largest influence ($Q_B > Q_A$ for BNT-BKT-BLT) similar to the hard-PZT ($Q_B > Q_A$ for hard-PZT) at high power levels.

Loss mechanism difference among PZT's and Pb-free piezoelectrics

We present an intuitive domain reorientation atomic models for explaining the difference of the piezoelectric loss contribution among Pb-based and Pb-free piezo-ceramics. Our speculation is based on the crystal structure differences among PbTiO_3 and BaTiO_3 . We assume that the spontaneous polarization is primarily contributed by the perovskite A-ion (Pb) shift in PbTiO_3 due to anisotropic large ionic polarizability of Pb^{2+} ion; while B-ion (Ti) shift is the largest contribution in BaTiO_3 , due to isotropic and spherical Ba^{2+} ion with closed electron shell. If we illustrate 90° domain wall models for both A-ion shift and B-ion shift spontaneous polarization materials, Fig. 46 may be obtained. As we discussed in Fig. 25, the piezoelectric loss may be correlated with Gauss Law, $\text{div} (D) = \sigma$ (charge). That means, the piezoelectric loss is a measure of the polarization alignment easiness from

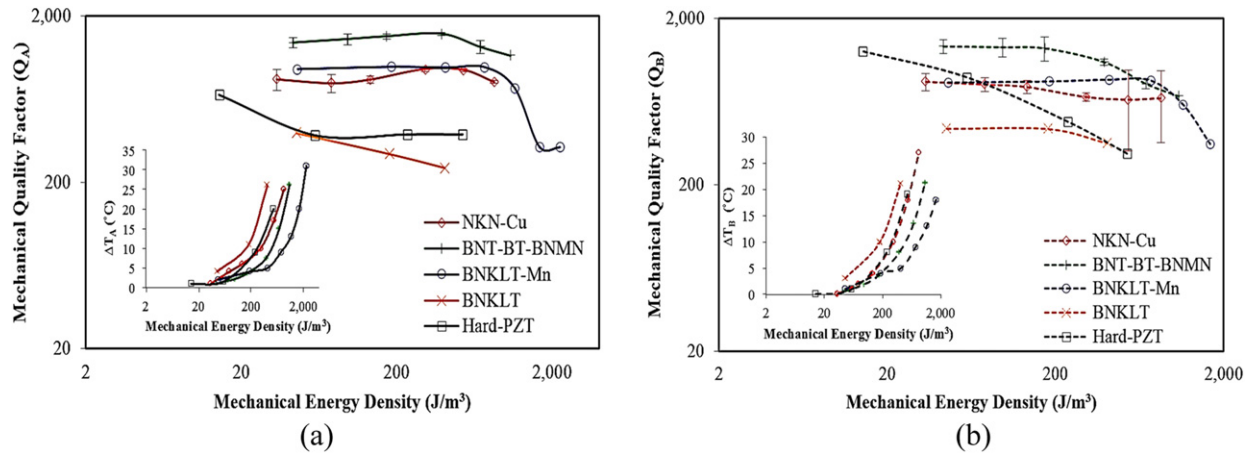


Fig. 45 Temperature rise and mechanical quality factors for (a) resonance (ΔT_A and Q_A) and (b) anti-resonance (ΔT_B and Q_B) as functions of mechanical energy density ($U_{mech} = \frac{1}{2} \rho v_{rms}^2$ or lead-free and hard-PZT piezoelectric ceramics).

the “head-to-head” or “tail-to-tail” to the “head-to-tail”. In the perovskite A-ion model piezoelectric, large size A-ions need to move largely with distorting the crystal frame during this reorientation process, which seems to require higher energy, leading to a large piezoelectric loss $\tan \delta$; while in the B-ion model piezoelectric, small size B-ion can easily move in a relatively large “rattling space” in a solid frame created by A-ions. This explains large intensive piezoelectric loss factor contribution in PZT, and small contribution in Pb-free piezoelectrics. Without conducting numerical simulation of the domain wall mobility and energy, the above is just an intuitive and speculative model.

Grain Size Effect on Hysteresis and Losses

Grain size dependence of pseudo-DC field induced strain

Grain size reduction usually exhibits finer domain size in polycrystalline ferroelectrics. Grain size reduction also increases the domain wall pinning, leading to the loss reduction. Fig. 47(a) shows the transverse field-induced strains of 0.8 at% Dy doped fine grain ceramic BaTiO₃ (grain diameter around 1.5 μm) and of the undoped coarse grain ceramic (50 μm), reported by Yamaji *et al.* (1977). As the grains become finer, the induced strain decreases and the hysteresis becomes smaller. This is explained by the increase in coercive field for 90° domain rotation with decreasing grain size. The grain boundaries (with many dislocations on the grain boundary) “pin” the domain walls and do not allow them to move easily. The decrease in grain size also seems to make the phase transition of the crystal much more diffuse. Although the effective value of d_{33} decreases in the Dy-doped sample, the temperature dependence is remarkably improved for practical applications. It should be noted that Yamaji’s experiment cannot separate the effects due to intrinsic grain size from ionic doping.

Thus, Uchino and Takasu studied the effects of grain size on PLZT (Uchino and Takasu, 1986). We obtained PLZT (9/65/35) powders by coprecipitation. Various grain sizes in the range of 1–5 μm were prepared by hot-pressing and by changing sintering periods, without using any dopants. Fig. 47(b) shows the dependence of the longitudinal field-induced strain on the grain size. As the grain size becomes smaller, the maximum strain decreases monotonically. However, when the grain size becomes less than 1.7 μm , the hysteresis is reduced. In conclusion, a decrease in the grain size reduces the induced strain and hysteresis.

Grain size dependence of high-power performance

Sakaki *et al.* (2001) studied the grain size effect on high power performances from a practical device application viewpoint. The vibration velocity versus the temperature rise was investigated for various grain size soft Nb-doped PZT’s from 0.9 μm to 3 μm . Soft PZT’s were intentionally chosen to enhance the grain size effect measurements. For two different grain sizes, 0.9 μm and 3.0 μm indicates that a higher maximum velocity of about 0.40 m/s is observed for the 0.9 μm -grain ceramic than that of the 3.0 μm -grain ceramic (0.30 m/s). Furthermore, the temperature rise for the fine grain ceramic is observed to be about 40% lower than the coarse grain ceramic near the maximum vibration velocity (0.30 m/s). This trend suggests that a higher vibration velocity and lower heat generation can be achieved by reducing the grain size, which has been confirmed by investigating the heat generation as a function of the grain size at various vibration velocities, shown in Fig. 48. A linear trend in heat generation can be found with grain size. In addition, the slope of heat generation is found to increase with an increment of the vibration velocity. This in turn suggests effective control over heat generation with lowering the grain size of ceramic.

It is known that a Nb-doped PZT with molecular formula $(Pb_{1-y/2} \square_{y/2})(Zr_xTi_{1-x-y}Nb_y)O_3$ is free of oxygen vacancies, hence, the movable space charge or impurity dipole may not be observed in this material. Thus, it is apparent that the increment of the mechanical quality factor (Q_m) with reducing the grain size is not caused by the space charge effect of oxygen vacancies, but by the grain size effect. Two origins can be speculated for the grain size effect: (1) The change in the configuration of the domain structure

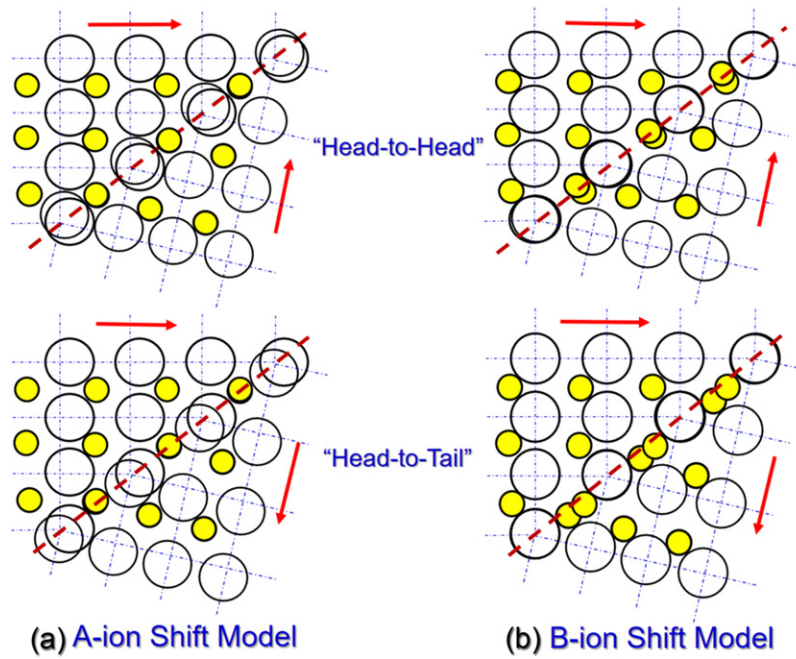


Fig. 46 Domain reorientation atomic models for explaining the piezoelectric loss. (a) A-ion shift model, (b) B-ion shift model.

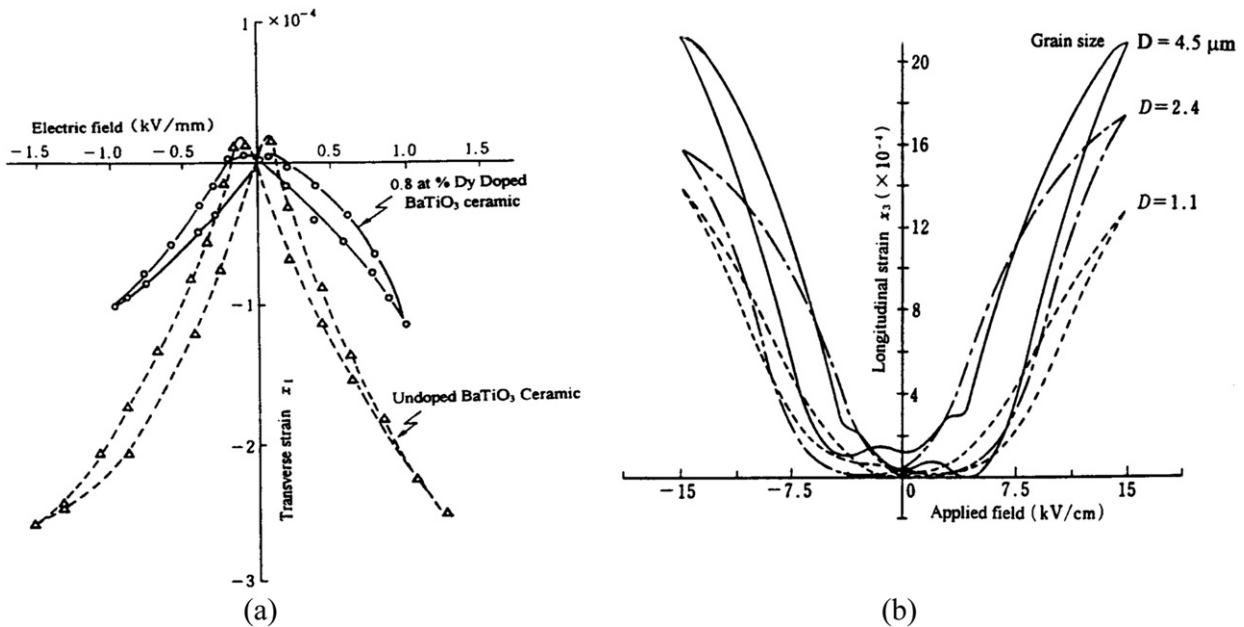


Fig. 47 (a) Electric field induced strain curves in Dy doped and undoped BaTiO_3 ceramic samples. (b) Grain size dependence of the induced strain in PLZT ceramics. Reproduced from Yamaji, A., Enomoto, Y., Kinoshita, E., Tanaka, T., 1977. Proc. 1st Mtg. Ferroelectr. Mater. Appl. 269 1977. Uchino, K., Takasu, T., 1986. Inspection 10, 29.

(smaller domain for a smaller grain), (2) The pinning effect by the grain boundaries with a reduction in the grain size (i.e., grain boundaries contribute as additional pinning points).

DC Bias Electric Field & Stress Effect on Losses

High-power piezoelectric devices, such as Langevin transducers, medical ultrasound transducers, etc., are usually working under external stress/electric field biases. Although the performance of these materials transducers has been thoroughly studied, there is a

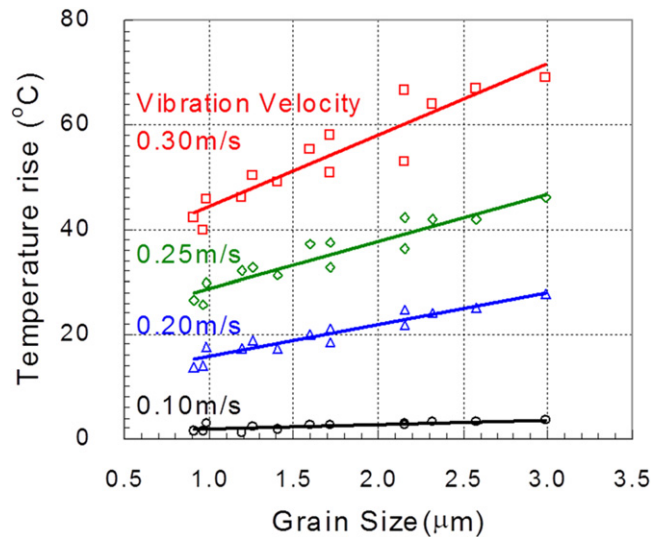


Fig. 48 Grain size dependence of the temperature rise of the PZT for various vibration velocity. Reproduced from Sakaki, C., Newarkar, B.L., Komarneni, S., Uchino, K., 2001. Grain size dependence of high power piezoelectric characteristics in Nb doped lead zirconate titanate oxide ceramics. Jpn. J. Appl. Phys. 40, 6907–6910.

lack of study on the fundamental piezoelectric loss parameters at high power conditions, which is important in the computer simulation in designing the optimum transducer configuration. A comprehensive study of loss mechanism under external biases can be both useful for enhancement of piezoelectric high-power applications and also it is beneficial for achieving a better understanding of loss mechanisms in general.

DC Bias Electric Field Effect on Losses

Internal bias field, which was attributed from acceptor defect clusters, plays important role in domain kinetics in “hard PZT”. In Section “Unidirectionally fixed dipole alignment”, we indicated that the “internal bias field” is observed in the high-power piezoelectrics, which seems to stabilize domain configuration (Gao *et al.*, 2007b). For acceptor (Fe^{3+}) doped PZT’s, a long (a couple of hours) “aging process” associated with the reorientation of the local defect clusters is required for obtaining a high internal bias field, which can suppress the amount of switchable polarization, leading to a dramatical increase in the mechanical quality factor Q_m .

Expecting a high-power performance improvement similar to the “internal bias field”, we examined the “external DC bias field” effect on hard and soft PZT k_{31} type rectangular plate specimens (Gao *et al.*, 2007b). Fig. 49(a) Top shows the Q_m value changes as a function of external positive DC bias for aged “hard” specimen PZT-PSM-Lu. After aging process the Q_m value was developed as high as 1660 already, by applying external positive bias the Q_m value increased by 18%. At the bias field level of 150 V/mm the Q_m value reached to 1900. The simultaneous k_{31} value measurement of the “hard” specimen in Fig. 49(a) Bottom shows only slight decrease in the k_{31} value of the PZT-PSM-Lu specimen.

On the contrary, Fig. 49(b) Top and Bottom show the Q_m and k_{31} value change for the “soft PZT”. Similar to the “freshly” poled specimens, the Q_m value of the PZT sample held unchanged at room temperature for 1 month after poling, which increases with increasing positive bias level; a significant increase by 35% was observed in the Q_m under DC bias field, which verifies our speculation on the loss suppression under DC bias field; while the k_{31} value change is very small with DC bias levels. Since no “long-term aging” related to the internal bias field development exists in the “soft PZT”, the Q_m and k_{31} values do not change even one month after poling.

Bansal *et al.* (2018). further clarified the stabilization mechanism of the ferroelectric performance under the DC bias electric field with respect to the three dielectric, elastic and piezoelectric losses. We mainly focused on the dependence of properties of the PZT k_{31} -type plates under different vibration velocity conditions as a function of external DC bias field, by comparing the results among hard and soft PZT’s. The paper titled “Effect of DC bias field on the complex materials coefficients of piezoelectric resonators” by Wang *et al.* (2003). did not provide sufficient information on three losses separately.

Continuous admittance spectrum method under DC bias electric field on the hard (PIC 144, PI Ceramic GmbH, Germany) and soft (PIC 255) PZT’s was used under the vibration velocity less than 0.030 m/sec, so that no heat generation more than 1°C was observed even at the resonance frequency range for both hard and soft PZT’s. Fig. 50(a) and (b) show the dielectric permittivity (at off-resonance frequency), dielectric loss; elastic compliance, elastic loss; piezoelectric constant, piezoelectric loss for Hard and Soft PZT’s, respectively. The dielectric constant ϵ_{33}^x change was - 0.8% for the hard PZT and - 1.7% per 100 V/mm for the soft PZT for a positive bias field and 0.5% for hard PZT and 1.2% for soft PZT in the case of a negative bias field. This may indicate a sort of threshold of the domain wall dynamics, suggesting a two-step mechanism. To the contrary, the intensive dielectric loss $\tan\delta$ (note one order of magnitude difference between the hard and soft PZT’s) shows a decreasing tendency with a positive DC bias field with a similar bend around 200 V/mm and an increasing tendency with a negative DC bias field. Though both specimens did not

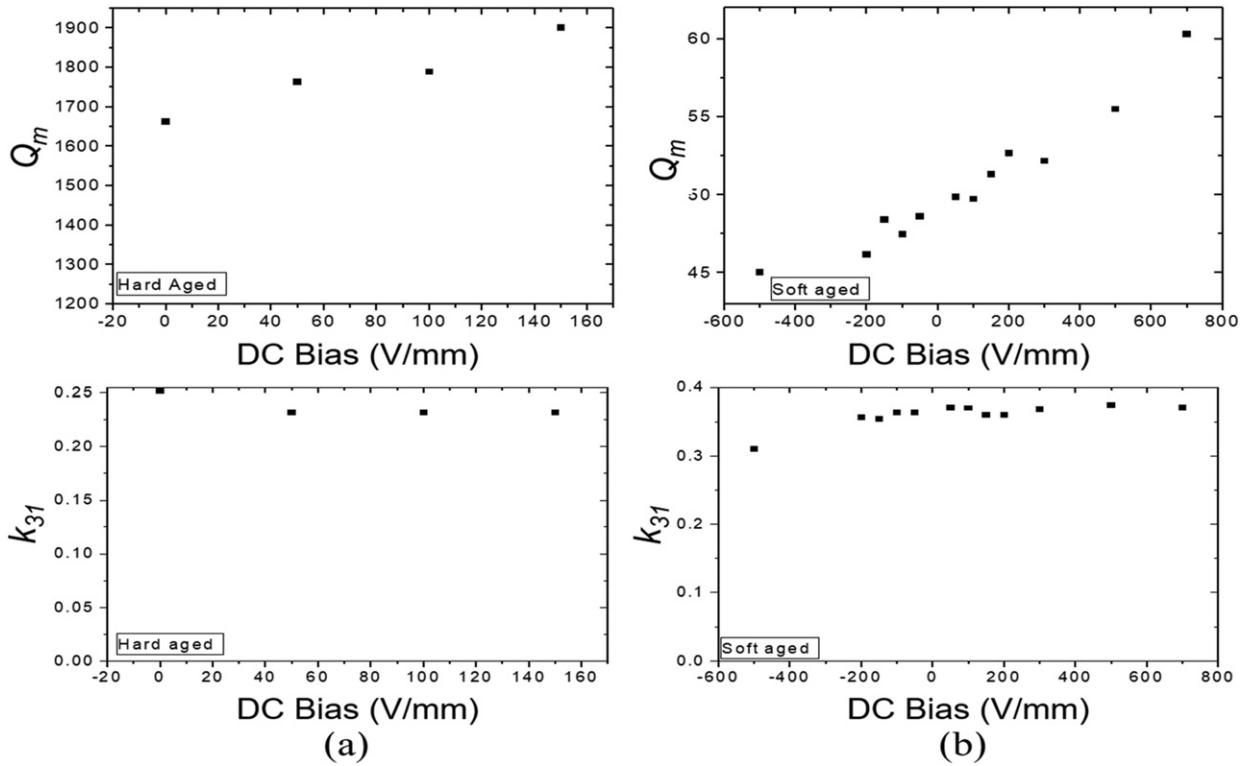


Fig. 49 DC bias electric field effect on the mechanical quality factor Q_m and electromechanical coupling factor k_{31} for (a) Hard PZT (aged) and (b) Soft PZT. Reproduced from Gao, Y., Uchino, K., Viehland, D., 2007b. Effects of thermal and electrical history on 'hard' piezoelectrics: A comparison of internal dipolar fields and external DC bias. J. Appl. Phys. 101 (5), 054109.

exhibit significant dielectric loss change, the change rate (-0.4% per 100 V/mm) of the hard PZT is less than the rate (-1.5% per 100 V/mm) of the soft PZT for a positive DC bias field.

The % change in elastic compliance s_{11}^E was -0.7% per 100 V/mm for the hard PZT, in comparison to -1.7% for the soft PZT for positive bias field and 0.5% for hard PZT and 1.4% for soft PZT in the case of negative bias field. The elastic compliance decrease with the positive DC bias field indicates that the PZT ceramics get elastically-hardened as the DC Bias field is applied whereas effect of negative DC bias field is completely opposite. The elastic loss $\tan\phi'$ (inverse of the mechanical quality factor at resonance) showed a shift of -1.1% per 100 V/mm for the hard PZT and -2.4% for soft PZT with increasing positive DC Bias field. Also, it showed a shift of 0.8% per 100 V/mm for the hard PZT and 1.9% for the soft PZT under negative DC bias field.

Regarding the piezoelectric constant d_{31} , the decrease for the hard PZT (-1% per 100 V/mm) was less than that for the soft PZT (-1.5% per 100 V/mm) under a positive DC bias field. Also, apart from the real parameter, piezoelectric loss change of the hard PZT was again smaller (-1.9% per 100 V/mm) for the hard PZT as compared to the soft PZT (-3.1%). For negative DC bias field, the piezoelectric constant magnitude increase for the hard PZT (0.7% per 100 V/mm) was less than for the soft PZT (1.2% per 100 V/mm). Apart from that, piezoelectric loss change of the hard PZT was again smaller (1.5% per 100 V/mm) as compared to the soft PZT (2.8% per 100 V/mm).

We provided the dependency of dielectric, elastic and piezoelectric coefficients (real parameters and imaginary losses) on the vibration velocity and DC bias field comprehensively. Note that as we drive the piezoelectric ceramic at a high vibration velocity, we are introducing AC stress in the material. A positive DC bias electric field affects in a way, that is, decrease in the dielectric constant, elastic compliance, piezoelectric coefficient and their corresponding losses, whereas a negative DC bias field affects in a completely opposite way. On the contrary, under the AC resonance vibration, the decrease rate of these physical parameters under small vibration level is enhanced under large vibration level. This situation can be visualized in the 3D plot in Fig. 51, showing the dependence of elastic loss $\tan\phi'$ on the externally applied DC bias field and the vibration velocity at the k_{31} sample length edge in the hard (PIC 144) and soft (PIC 255) PZT. In comparison with a relatively smooth plane contour for the soft PZT, a clear bend on the contour plane is observed for the hard PZT, which suggests two stage domain wall dynamic mechanism (discussed already in Fig. 16). We can find that the intensive elastic loss $\tan\phi'$ shows two different trends under vibration velocity and DC bias field; increase with the vibration velocity (180° domain wall destabilization) and decrease with positive DC bias field (domain wall stabilization). Roughly speaking, the vibration velocity 100 mm/s ($+3\%$ and 5% change in s_{11}^E for the hard and soft PZT's) exhibits the almost equivalent "opposite" change rate ($-1.7\% \times 2$ and $-2.3\% \times 2$ change in s_{11}^E for the hard and soft PZT's) of 200 V/m DC electric field. That is, the heat generation under a high vibration level can be suppressed by the bias electric field application.

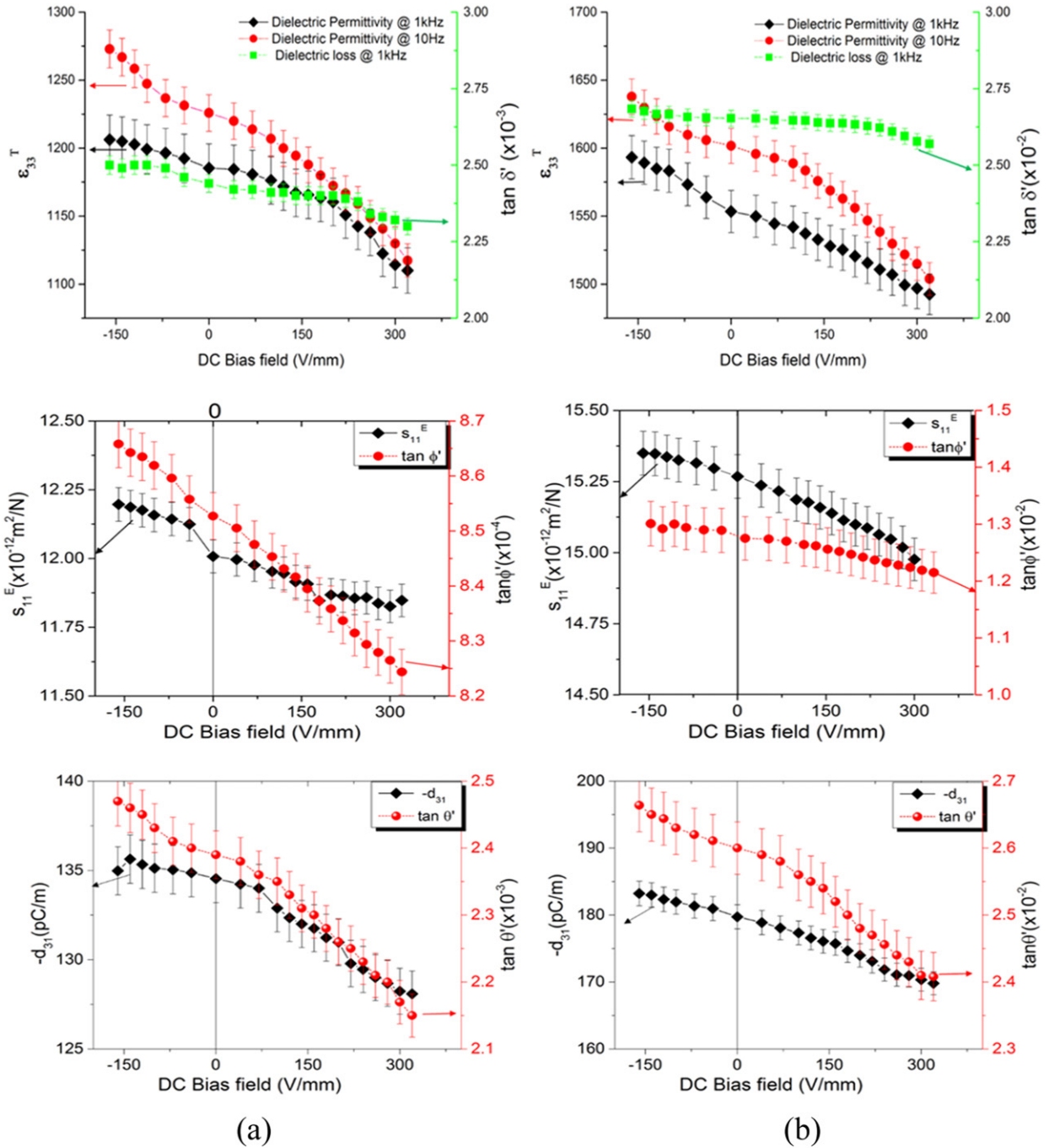


Fig. 50 DC bias electric field effect on permittivity, elastic compliance, piezoelectric constant and their respective losses for (a) Hard PZT (aged) and (b) Soft PZT. Reproduced from Bansal, A., Shekhani, H., Majzoubi, M., *et al.*, 2018. Improving high power properties of PZT ceramics by external DC bias field. *J. Am. Ceram. Soc.* 101.

DC Bias Stress Effect on Losses

High power piezoelectric devices are often subjected to external mechanical constraints or biases, in many applications such as underwater transducers. While their performance and property changes under these external biases have been widely investigated by different researchers (Zhang and Zhao, 1999; Zhou *et al.*, 2004; Krueger, 1967; Zhang *et al.*, 1997; Yimnirun *et al.*, 2006; Unruan *et al.*, 2010; Yang *et al.*, 2000) from a practical application viewpoint, there is a significant lack of fundamental research on the loss mechanism in terms of three existing losses (dielectric, elastic, and piezoelectric) under external stress bias. Daneshpajoo *et al.* reported reliable data on the DC bias stress effect of these three losses, including their unique measuring technique (Daneshpajoo *et al.*, 2019).

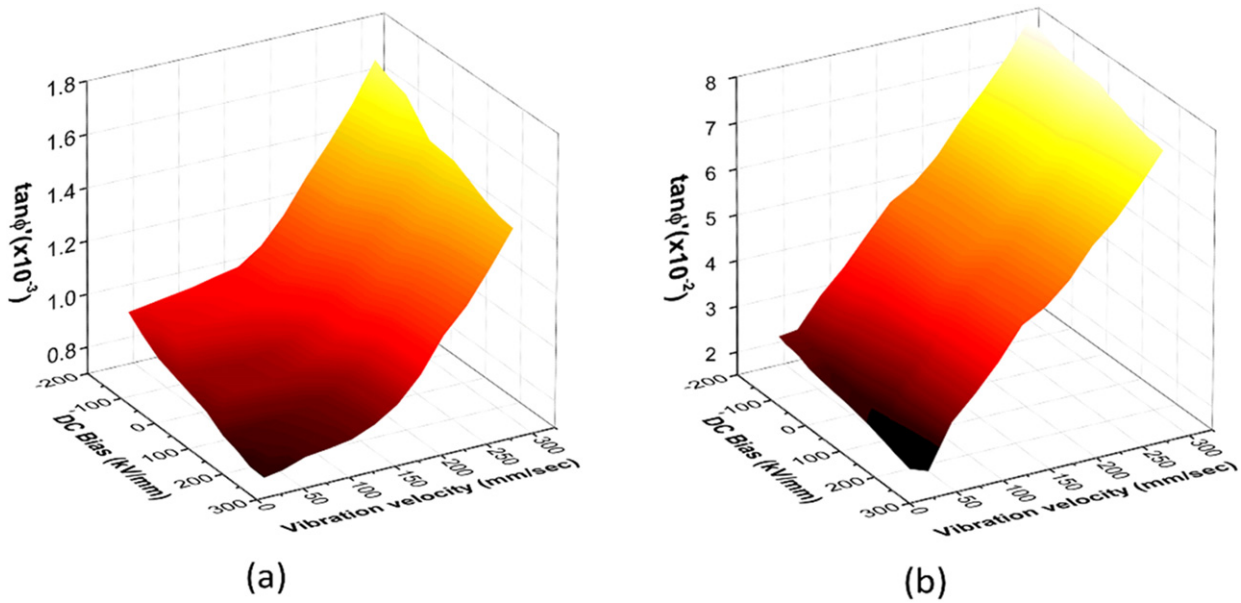


Fig. 51 3D plot showing the variation of elastic loss for PZT's as a function of DC Bias field and vibration velocity for (a) Hard PZT (b) Soft PZT. Reproduced from Bansal, A., Shekhani, H., Majzoubi, M., *et al.*, 2018. Improving high power properties of PZT ceramics by external DC bias field. J. Am. Ceram. Soc. 101..

Bolt-clamped langevin transducer

In order to investigate the effect of uniaxial stress, two different configurations can be used; quasi-static and resonant (Lynch, 2010; Damjanovic, 1997; Hall, 2001). Although proposed methodologies based on these configurations were able to capture the piezoelectric material real part property changes under compressive stress, they have suffered from the difficulty in studying the piezoelectric loss mechanism (i.e., imaginary performance) at the resonance condition, due to the experimental complications. In studying the compressive mechanical bias stress dependence of the loss mechanism, Daneshpajoo *et al.* adopted a modified bolt-clamped Langevin transducer, which consists of mass/load, active PZT and inactive PZT parts, so that the admittance spectrum can be obtained including the stress applying jig. A symmetric configuration was chosen to provide a symmetrical and uniform AC-stress distribution over the active PZT samples (center 6 ring specimens), shown in Fig. 52. The inactive/dummy PZT samples (side 2×2 inactive rings) were introduced to increase the length/thickness ratio of structure and reduce the AC stress nonuniformity. The structure was designed in a way that the fundamental longitudinal-resonance is far from higher resonance frequencies and therefore no interference or spurious modes would be expected by applying external load on the samples, and that a uniform AC-stress ($X_{33}^{AC,rms}$) and DC-stress (X_{33}^{DC}) distribution along the longitudinal direction on the active 6 PZT rings (less than $\pm 10\%$ for AC stress and less than 0.1% for DC stress). A soft piezoelectric $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PIC-255, PI Ceramic GbmH, Germany) was intentionally chosen from a scientific viewpoint, and an equivalent circuit methodology with three losses based on the fundamental longitudinal-mode was developed with symmetrical head and tail masses to facilitate the analysis on a modified bolt-clamped Langevin transducer. Since very small clamping stress exhibits unstable measuring results, we adopted stress range 20–42 MPa in the experiments.

DC Bias Stress Dependence of Physical Parameters & Loss Factors

Fig. 53 summarizes the dependence on the compressive stress along the polarization direction of (1) intensive dielectric constant ϵ_{33}^E and dielectric loss $\tan\delta'$; (2) intensive elastic compliance (s_{33}^E) and elastic loss ($\tan\phi'_{33}$); (3) piezoelectric constant (d_{33}) and intensive piezoelectric loss ($\tan\theta'_{33}$); (d) piezoelectric coupling factor (k_{33}) and its corresponding loss. The permittivity shows a monotonic increase under compressive stress (+3.67% increase at maximum stress level 42 MPa), while the dielectric loss decreases slightly with an increase of compressive stress along polarization direction (−3.6% decrease at maximum stress level 42 MPa). The elastic compliance shows a monotonous decrease (i.e., stiffening) behavior under compressive stress (+2% increase at maximum stress level 42 MPa). Also, similar to the dielectric loss, the elastic loss decreases remarkably under compressive stress (−12% at maximum stress level). While the piezoelectric constant shows a small increase under compressive stress (1% at highest stress level), the intensive piezoelectric loss showed considerable increase ($\sim 12\%$ at highest stress level). It is intriguing to mention the piezoelectric coupling factor (k_{33}) behavior, which keeps almost constant over small compressive stress range; while the electromechanical coupling loss factor ($2\tan\theta'_{33} - \tan\phi'_{33} - \tan\delta'_{33}$) is increasing with an increase of compressive stress. While the piezoelectric constant and coupling factor of soft PZT do not show a major change, the loss parameters, especially elastic loss, show a considerable improvement. The decrease in elastic loss under compressive stress (which indicates lower heat generation),

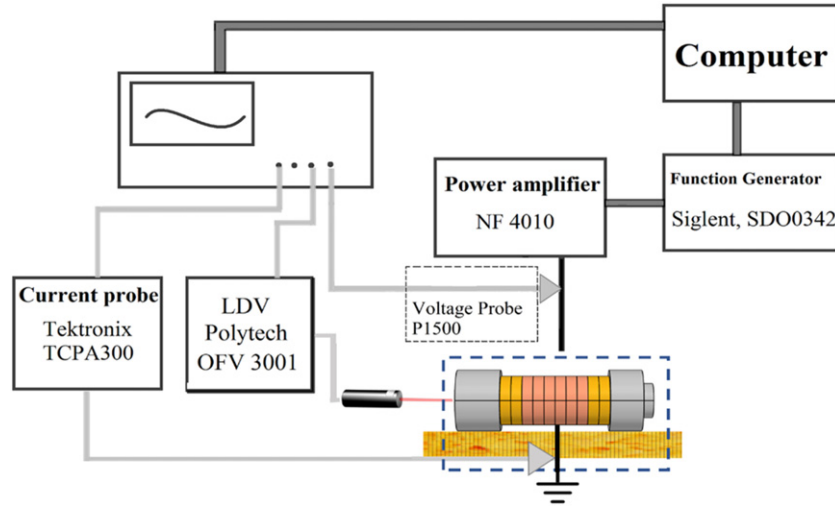


Fig. 52 Schematic experimental setup for measuring DC bias stress effect on the Langevin transducer.

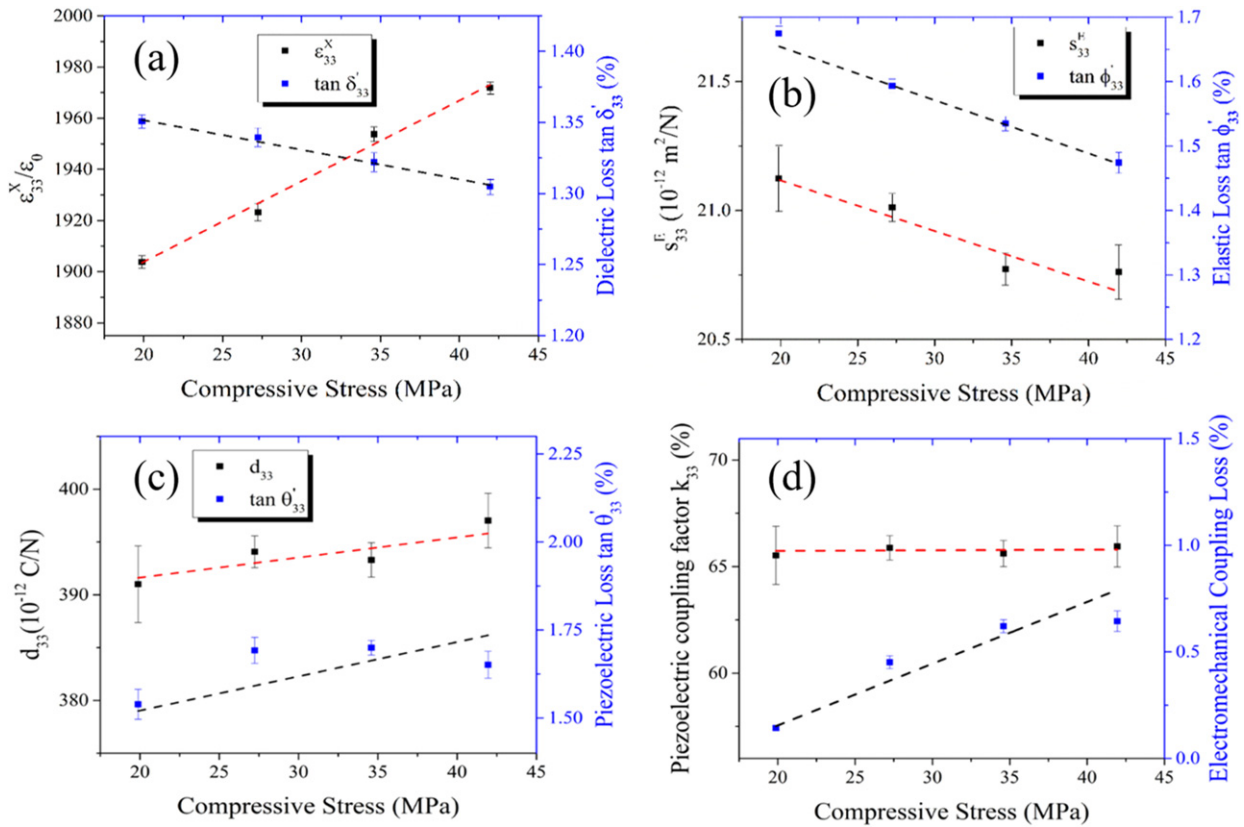


Fig. 53 Dependence on the compressive stress along the polarization direction of (a) intensive dielectric constant ϵ_{33}^E and dielectric loss $\tan \delta_{33}'$; (b) intensive elastic compliance (s_{33}^E) and elastic loss ($\tan \phi_{33}'$); (c) piezoelectric constant (d_{33}) and intensive piezoelectric loss ($\tan \theta_{33}'$); (d) piezoelectric coupling factor (k_{33}) and its corresponding k_{33}^2 loss. Reproduced from Daneshpajoo, H., Choi, M., Park, Y., *et al.*, 2019. Compressive stress effect on the loss mechanism in a soft piezoelectric $\text{Pb}(\text{Zr,Ti})\text{O}_3$. Rev. Sci. Instrum. 90. Available at: <https://doi.org/10.1063/1.5096905075001>.

in conjunction with stable piezoelectric constant over low stress levels, can provide higher mechanical quality factor Q_m , very beneficial for piezoelectric resonance/high power applications.

In a brief summary, the positive DC electric field and compressive (negative) stress exhibit a similar decreasing trend in real and imaginary physical parameters such as permittivity, elastic compliance and piezoelectric d constant, and their corresponding loss factors, as well-known empirical facts such as “superior performance of the bolt-clamped Langevin

transducers". However, the loss change trend under the DC bias electric field or stress cannot be understood microscopically at present. We need to wait for a detailed loss mechanism model.

Conclusions

The bottleneck of the miniaturization of high-power piezoelectric devices is the heat generation originated from various losses: (1) piezoelectric material's loss, (2) multilayer structure loss (e.g., electrode loss), and (3) drive/control circuit loss. This article focused on the material's losses.

- (1) There are three loss origins in piezoelectrics: the dielectric, elastic and piezoelectric losses. The 180° and non- 180° domain wall motions contribute primarily to the extensive dielectric and elastic losses, respectively. To the contrary, the piezoelectric loss is a sort of "hidden loss", which cannot be separately observed. When we consider the direct effect, for instance, we presume that 90° domain wall motion includes two steps; Step 1: under the external tensile stress, "ferroelastic alignment" occurs, so that the 90° domain wall will move with time delay by $\tan\phi'$. Step 2: according to the lattice cell tetragonal shape alignment, the polarization reorientation follows, which is called "electromechanical coupling alignment"; that is, input mechanical energy is converted to electrical energy by the rate of electromechanical coupling factor square k^2 with the time delay by $(2\tan\theta' - \tan\delta' - \tan\phi')$. Note that there are two possibilities of the polarization reorientations; upward or downward. In a highly-resistive specimen, the "Gauss Law", $\text{div}(D) = 0$ (no free charge) generates the motive force from the "head-to-head" or "tail-to-tail" to the "head-to-tail" domain configuration. The resulting superposed loss for the direct effect is expressed as $(2\tan\theta' - \tan\delta')$.
- (2) We introduced three loss-measurement techniques for separately measuring dielectric, elastic and piezoelectric losses: quasi-DC, resonance drive, and pulse/burst drive methods.
- (3) Heat generation occurs in the piezoelectric specimen uniformly under an off-resonance mainly due to the "intensive dielectric loss"; while heat is generated primarily at the vibration nodal points via the "intensive elastic loss" under a resonance. In both cases, the loss increase is originated from the "extensive dielectric loss" change with electric field and/or stress above a certain critical field or stress.
- (4) In Pb-base piezoelectric perovskites such as PZTs, the mechanical quality factor Q_B for the antiresonance (B-type) mode is higher than Q_A for the resonance (A-type) mode. $Q_A < Q_B$ indicates that intensive piezoelectric loss $\tan\theta'$ is larger than the average of the elastic $\tan\phi'$ and dielectric $\tan\delta'$. Since the maximum vibration velocity is also higher for the antiresonance mode than for the resonance mode, we proposed the antiresonance usage for the motor, transformer and transducer applications.
- (5) After determining the mechanical quality factor Q_m between the resonance and antiresonance frequencies using the precise real electric power method, the maximum Q_m was discovered at a frequency between the resonance and antiresonance points. We proposed thus an "inductive drive method" for realizing the maximum efficiency in piezoelectric transducers/motors.
- (6) Pb-free piezoelectric perovskites exhibit $Q_A > Q_B$ or $Q_A \approx Q_B$, which suggests that the contribution of the intensive piezoelectric loss $\tan\theta'$ is not large in Pb-free piezoelectrics.
- (7) Actuator materials: Doping rare-earth ions into PZT-Pb(Mn,X)O₃ (X = Sb, Nb) ceramics increases the maximum vibration velocity (RMS) up to 1 m/s in a rectangular k_{31} type specimen, which corresponds to one order of magnitude higher energy density ($\sim 50\text{W}/\text{cm}^3$) than conventionally commercialized piezo-ceramics ($\sim 5\text{W}/\text{cm}^3$). To obtain high power density/high vibration velocity materials, domain wall immobility/stabilization via the "positive internal bias field" seems to be essential, rather than the local "domain wall pinning effect".

Though we discussed the microscopic loss mechanisms in terms of 180° and 90° (or non- 180°) domain wall dynamics, all analyses are yet just speculations. Experimental domain motion observations on single crystals such as barium titanate and PMN-PT are highly anticipated from the scientific viewpoint. On the other hand, from the industrial viewpoint, the development of high-power piezoelectric materials as high as $100\text{W}/\text{cm}^3$ will be the final target, especially for thin/thick PZT film (i.e., low volume) MEMS applications.

Acknowledgment

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Piezoelectric Energy Harvesting for Low-Power Smart Electronics

Saichon Sriphan, King Mongkut's University of Technology North Bangkok, Rayong, Thailand and Advanced Materials Research Unit, Department of Chemistry, School of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand

Thitirat Charoonsuk, Advanced Materials Research Unit, Department of Chemistry, School of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand and Department of Materials Science, Srinakharinwirot University, Bangkok, Thailand

Tosapol Maluangnont, Electroceramics Research Laboratory, College of Materials Innovation and Technology, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand

Naratip Vittayakorn, Advanced Materials Research Unit, Department of Chemistry, School of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand and Department of Chemistry, School of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand

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Abstract

In recent years, significant progress regarding energy harvesting has been made, owing to the need to replace conventional energy sources with alternative, green, and sustainable ones. Among them, mechanical energy harvesting is a promising strategy with outstanding characteristics of high conversion efficiency, facile fabrication process, simple structure, flexible selection of materials, and the ability to capture energy independent of season. Nowadays, the piezoelectric mechanism has gained attention from the research community as a prominent mechanical energy harvesting method. Diverse technologies in harvesting and sensing schemes have been innovatively developed alongside explorations of novel piezoelectric materials and the establishment of theoretical foundations. This article comprehensively reviews piezoelectric energy harvesting from the research background to its significance. The operation mechanisms of a piezoelectric nanogenerator (PENG) in various modes, including the theoretical principle of piezoelectricity, are discussed. Three generations of piezoelectric material development are explained, including structural designs of PENG for specific applications. Finally, highlighted applications of PENG in diverse fields such as energy harvesting and sensing, biomedical electronics, and novel intelligent sensing technologies, have been reviewed.

Key Points

- The basic operating mechanisms, and related theoretical principle of PENG are presented.
- Generations of piezoelectric material development is discussed.
- Structural designs, highlight applications, and prospects for development of PENG are introduced.

Introduction

It is undeniable that the number of interconnected electronic devices increases exponentially every year. These devices can communicate with others in any place at any time, thanks to the rapid advance in wireless sensor networks (WSNs), sensor/actuator technology, and low-power smart electronic devices (Shaikh and Zeadally, 2016). Internet of Things (IoT) and wearable electronic devices are becoming a new paradigm that facilitates and improves everyday life for human beings. The primary energy supply sources, such as alkali coin cell or rechargeable Li-ion coin cell batteries, are utilized mostly for portable/flexible electronics devices. However, due to their inflexibility, relatively heavyweight, limited lifetime, and inconvenience of replacement, bulk batteries might not be an answer in advanced applications such as IoT and smart flexible electronic devices. Only a limited amount of Li-ion batteries is recycled nowadays; most of the waste batteries end up in landfills which is a serious pain point for sustainability (Melchor-Martínez *et al.*, 2021). Consequently, clean energy harvesting from the ambient environment and a self-sustaining electronic system have become increasingly attractive in the worldwide energy market. Fig. 1 represents the classification of energy harvesting sources. Traditional renewable sources have been developed, such as hydroelectric, geothermal, and wind power. Nevertheless, these technologies are inappropriate for collecting and utilizing small mechanical energy for portable/flexible electronic devices due to several reasons such as incompatibility with integrated circuits, reliability, large size, and inflexibility.

Recently, energy harvesting technologies such as photovoltaic (PV) cell, electromagnetic (EM) generator, thermoelectric (TE) cell, pyroelectric (PyE) cell, triboelectric nanogenerator (TENG), and piezoelectric nanogenerator (PENG) have emerged as a potential solution for self-powered micro/nano-systems, capable of accelerating the rapid development of IoT and smart wearable devices in daily life (Akin-Ponnle and Carvalho, 2021; Shi *et al.*, 2021; Pang *et al.*, 2021). Table 1 summarizes the strengths and weaknesses of emerging nanogenerator technologies. Each technology has its own advantages and critical issues. The PV cell technology exhibits high power-conversion efficiencies and excellent stability, but it has the limitation of harvesting time and high dependency on the environment (Nayak *et al.*, 2019; Tawalbeh *et al.*, 2021). To achieve a high output performance, the PV cell requires a complex structure as well as a large size, resulting in a heavyweight. The EM generator has a distinctive point in unlimited working time if the magnet and coils are paired following Faraday's law of induction (Cho and Kim, 2017). However, its

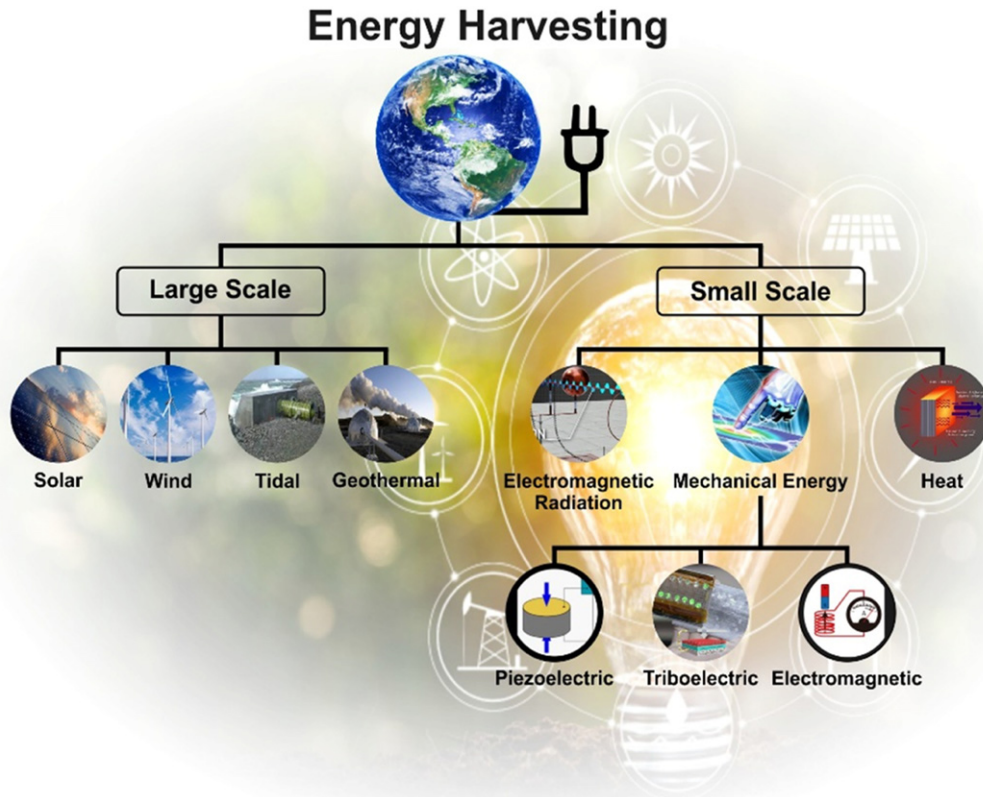


Fig. 1 Classification of energy harvesting technology in terms of energy level.

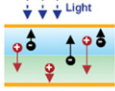
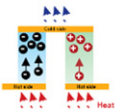
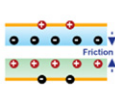
output performance, weight, portability and stretchability are critical issues for flexible electronic applications. Meanwhile, the TE cell can generate electric energy by using the difference in temperature between the human body and the ambient under the principle of the Seebeck effect of thermoelectric materials (Zoui *et al.*, 2020). Still, thermoelectric module performance highly depends on the temperature gradient, thermoelectric material performance, heat flux, and so on. The hugely generated heat flux from the human body is challenging issue for this technology. In addition, the PyE cell is another thermal energy harvester, which shows dominant advantages in simple structural design, lightweightness, and ability to make a flexible structure. This cell can be polarized electrically, due to permanent dipoles inside a pyroelectric material upon temperature change (Thakre *et al.*, 2019). Nevertheless, the amount of charge produced is rather low and unsuitable for energy harvesting. Recently, a new mechanical energy harvester known as a triboelectric nanogenerator (TENG), was developed. This lightweight, highly flexible device produces an outstanding output voltage with a facile structural design (Luo and Wang, 2020; Parida *et al.*, 2019). The operation mechanism of the TENG is based on the coupling of triboelectrification and electrostatic induction, thereby producing a stable AC signal in response to cyclic mechanical stimulations. Unfortunately, the generated output current by a TENG device is rather small, due to a high charge screening effect and a low amount of charge induction. Focusing on PENG, its working mechanism for electricity generation is similar to that of the PyE cell. Piezoelectric charges, which originate from electric dipoles, can be generated from stress which is applied to the device (Briscoe and Dunn, 2015; Liu *et al.*, 2020). PENG can be fabricated taking into account the flexibility, portability, and design simplicity for various smart applications. Like PyE cell, the electrical outputs of PENG are not high enough for driving electronic devices, requiring further improvement for the next stage of energy harvesting technology, as will be discussed throughout this article.

In 2006, Prof. Zhong Lin Wang (Wang and Song, 2006) proposed the concept of a micro-nano energy harvesting device called “nanogenerator”, based on Maxwell’s displacement current as the driving force for converting small-scale mechanical energy into electrical energy. Mechanical energy is one of the most common forms of energy. It is the sum of kinetic energy and potential energy, and is used to describe the ability of an object in performing work. Various forms of mechanical energy occur all the time in daily life such as natural movement and vibration, motion of living things at several levels, and industrial machinery.

Energy harvesting efficiency (η_{ME}) can be described in terms of output electrical energy (E_E) divided by the total input of mechanical energy (E_M). The η_{ME} , E_E , and E_M are defined by the following equations:

$$\eta_{ME} = \frac{E_E}{E_M} \times 100\% \quad (1)$$

Table 1 Comparison of important factors for various energy harvesting technologies

Energy harvesters*	Schematic	Output performance	Operating time	Size & weight	Flexibility	Stability & durability	Complex design & fabrication
PV cell		↑	↕	↑	↕	↑	↑
EM generator		↓	↑	↑	↓	↑	↓
TE cell		↕	↕	↑	↓	↕	↑
PyE Cell		↓	↕	↓	↑	↓	↓
TENG		↑	↑	↓	↑	↓	↓
PENG		↓	↑	↓	↑	↕	↓

*PV = Photovoltaic, EM = Electromagnetic, TE = Thermoelectric, PyE = Pyroelectric,

TENG = Triboelectric nanogenerator, PENG = Piezoelectric nanogenerator



Tendency to high value



Tendency to middle value



Tendency to low value

$$E_E = \int_0^{\Delta t} F \cdot d(t) dt \quad (2)$$

$$E_M = P \Delta t = I^2 R \Delta t \quad (3)$$

where F is the applied force, d is the moving distance while the force is being applied, Δt is the generation time, P is the output power, I is the current, and R is the resistive load connected to the harvester.

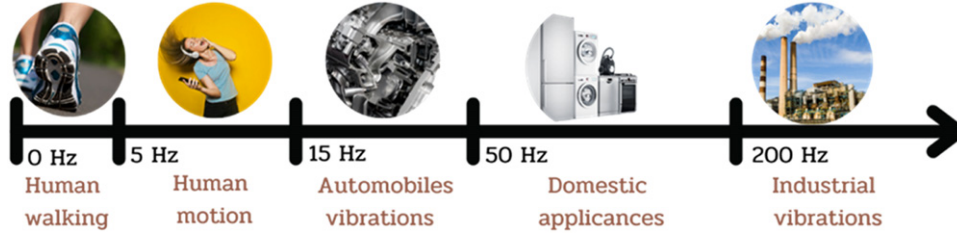


Fig. 2 Frequency of working range by different mechanical energy sources.

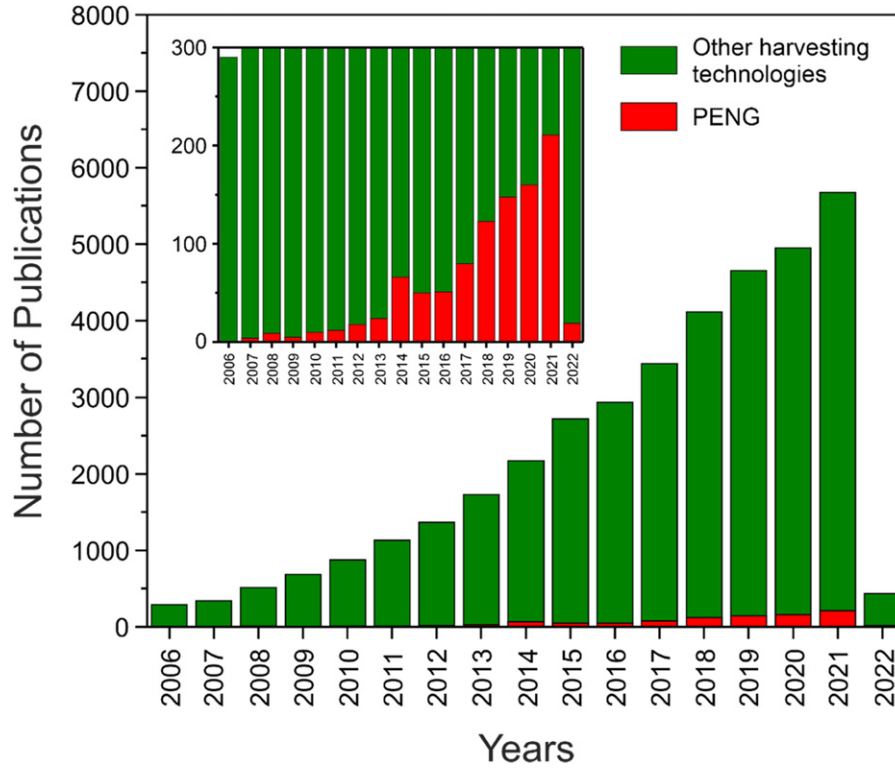


Fig. 3 Number of publications between the PENG and other energy harvesting technologies. Data obtained from Scopus database, January 14, 2022.

The biomechanical motion can be harvested and converted to electrical outputs using the piezoelectric effect. The harvested power density (P_{res}) for mechanical energy depends proportionally on the magnitude and motion frequency:

$$P_{res} = 4\pi^3 m \gamma Z_{max} f_{res}^3 \quad (4)$$

where m is the inertial mass, γ is the vibration amplitude of matter, Z_{max} is the maximum displacement, and f_{res} is the resonance frequency. **Fig. 2** displays the frequency level in different working ranges of mechanical energy sources. It is evident that PENG technology is appropriate for harvesting/sensing in low frequency applications (< 5 Hz), while a higher range better suits TENG operated in a rotating mode and an EM generator.

Among other harvesting technologies, PENG represents one of the primary groups of emerging methods for effectively harvesting ambient mechanical energy by utilizing the piezoelectric effect of material. PENG mechanism for harvesting is straightforward and simple, and based on the intrinsic polarization of piezo-materials. It does not require the use of magnetic field with separate voltage source and contact with other materials, as in the case of electromagnetic, electrostatic and triboelectric energy harvesting. It is also durable, reliable, lightweight, structurally compact in manufacturing, easily integrated into microelectromechanical systems, and less affected by environmental factors such as humidity. These remarkable properties are the reason why PENG technology has been continuously developed and improved when compared with other harvesters (Liu *et al.*, 2020; Pang *et al.*, 2021; Shi *et al.*, 2021), as shown in **Fig. 3**.

In this article, a comprehensive review of PENG with a special focus on the origin of piezoelectricity, fundamental theories of piezoelectric effect and piezoelectric-based devices, development of piezoelectric materials, structural designs, and potential applications are summarized. Firstly, some essential background and the significance of energy harvesting research related to the

Table 2 Crystalline properties of centro- and noncentro-symmetric crystals

Crystal system	Symmetry elements	Without piezoelectricity (centro-symmetric)	With piezoelectricity (Noncentro-symmetric)
Cubic	Center, axis, plane	m3, m3m	23, $\bar{4}3m$, 432
Tetragonal	Center, axis, plane	4/m, 4/mmm	4, 4, 422, 4 mm, $\bar{4}2m$
Rhombohedral	Center, axis, plane	$\bar{3}$, $\bar{3}m$	3, 32, 3 m
Orthorhombic	Center, axis, plane	mmm	222, mm2
Hexagonal	Center, axis, plane	6/m, 6/mmm	6, 6, 622, 6 mm, $\bar{6}m2$
Monoclinic	Center, axis, plane	2/m	2, m
Triclinic	Center	$\bar{1}$	1

piezoelectric effect are presented. Then, the fundamentals of piezoelectricity and relationship between a symmetry of the crystals and piezoelectricity are introduced. Working mechanisms of PENG in various modes are next discussed. Following that, piezoelectric materials for PENG are classified into three generations: (1) piezoelectric oxide nanostructures, (2) synthetic piezoelectric polymers and composites, and (3) organic piezoelectric materials and composites. Review of recent works on structural designs and potential applications of PENG are illustrated in detail.

Fundamentals of the Piezoelectric Effect

Piezoelectricity

In 1880, the brothers, Pierre and Jacques Curie, were the first to discover electric charges that appeared on several parts of quartz single crystals which are oriented in different directions. This phenomenon was named piezoelectricity, which comes from Greek and means “electricity by pressure” (“piezo” means pressure in Greek). Piezoelectricity is a natural phenomenon that couples the mechanical and electrical state of dielectric materials, which belong to the class of noncentro-symmetric crystals. Table 2 shows crystal class, symmetry elements, centro-symmetric and noncentro-symmetric point groups in crystals.

The piezoelectricity phenomenon describes the relations between mechanical strains on non-centrosymmetric crystal containing cation and anion crystalline lattices, and the resulting electrical behavior from the changes in electric polarization under deformation (Ramadan *et al.*, 2014; Covaci and Gontean, 2020). When piezoelectric materials are subjected to external strain such as pressure/stress in different directions, electric polarization in the crystal changes depending on orientation. Accordingly, positive and negative charges are developed on opposite faces of the crystal, resulting in an electric field (Mishra *et al.*, 2019). This phenomenon is called the “direct piezoelectric effect” (Fig. 4(a)). To produce electrical signals, a piezoelectric material is sandwiched between two electrodes connected to a resistance load R_L . Three possible directions of pressure/stress can be applied to piezoelectric materials: vertical, horizontal and shear modes. There is no stress at the original state, resulting in no charge transfer to the external load. However, when the force F_y is applied vertically to the piezoelectric material (Fig. 4(a)-i), the stress separates the center of gravity from the cations and anions. This creates dipole moment and polarization of piezoelectric material. In this case, the cation is compressed and the neighboring anions move away, thus generating positive and negative charges, respectively, on the top and bottom region close to the material surfaces. Polarization density depends on the applied force intensity that is stress. During compression, the induction of opposite charges stabilizes the piezoelectric material to neutral. This generates the piezoelectric current, I_p , which flows through the circuit. Now, let us consider the opposite situation when a piezoelectric material is subjected to tensile stress, *i.e.*, the piezoelectric material is stretched. The middle cation moves away to the top, thus changing the direction of polarization when compared with the compression stage. Alternatively, the external force, F_x , can also be applied to piezoelectric materials in a lateral direction (Fig. 4(a)-ii). The process of producing electric current is similar to that of vertical mode. Expanding piezoelectric material in X-direction leads to the generation of polarization in the same manner as compression in vertical mode, and creates I_p in the counterclockwise direction. In contrast to external stress compressed into material, negative charges are stored close to the top surface, thus generating current in the opposite direction of the tension mode. In addition, shear stresses can be applied to piezoelectric material. This leads to distortion of the material, which affects the re-arrangement of the crystalline lattice. When shear stresses focus on the top and bottom surfaces in clockwise directions, positive charges are created on the top region of piezoelectric materials (Fig. 4(a)-iii). This is distinct from the case in which the shear stress applied in counterclockwise direction, generating negative charges on the top surface. A variety of forces can be applied to piezoelectric materials to generate electrical signals. Thus, PENG finds diverse sensing applications, *e.g.*, healthcare, sport and security (Sun *et al.*, 2021; Cao *et al.*, 2021; Liu *et al.*, 2020).

The reverse action of applying an external electric field to the crystals to convert electrical energy into mechanical energy is known as the “indirect piezoelectric effect”. Here, an external field causes asymmetric displacements of anions and cations with net deformation of the crystal. The resulting strain is directly proportional to the applied electric field. The strain in a piezoelectric crystal is compressive or extensive, depending on the polarity of the applied field. As shown in Fig. 4(b), a positive and negative bias can be applied to a piezoelectric material. There are no charge transfers in its original state, due to the open-circuit of the power supply, V_s . With the application of voltage delivering positive charges to the top of the piezoelectric material (Fig. 4(b)-i), dipole orientation tends to be squeezed, thus decreasing the thickness of material, d_1 , when compared with the initial value, d_0 ($d_1 < d_0$). The piezoelectric material can be expanded when negative bias is applied (Fig. 4(b)-ii). Negative charges are stored on the top electrode. In this case, the thickness d_2 is larger than the initial one ($d_2 > d_0$). If an AC voltage is applied to the

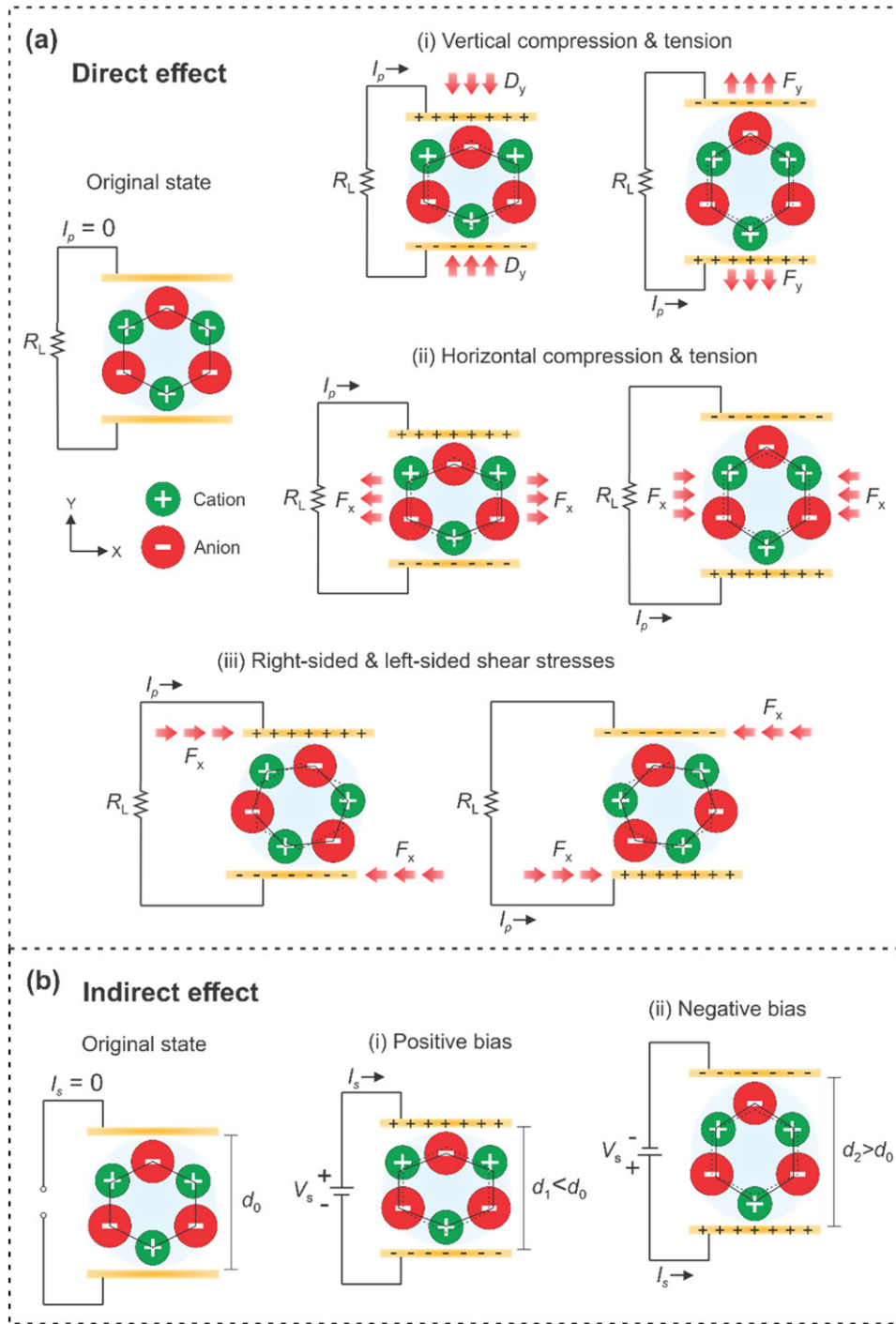


Fig. 4 (a) Direct and (b) indirect effects of piezoelectric materials.

specimen, the piezoelectric material is periodically subjected to positive and negative bias with controlled frequency. This can be utilized for actuators generating sound waves for buzzer and speaker (Mohith *et al.*, 2020; Kim *et al.*, 2011).

Mathematical Formulation of the Piezoelectric Effect

The mathematical formulation of piezoelectric effect relates to the response of a piezoelectric material to the applied mechanical strain (or stress) and electric field through polarization change (Fig. 5). This corresponds to direct and indirect piezoelectric effects, which can be utilized in diverse applications of sensors and actuators.

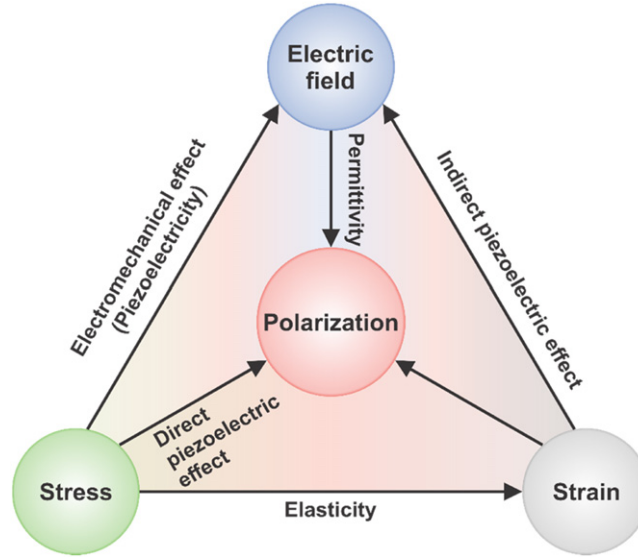


Fig. 5 Relations of piezoelectric effect.

The foundation is based on the linear behavior of piezoelectric material at low applied stress and electric field levels (Priya *et al.*, 2017; Ikeda, 1990). For the direct piezoelectric effect (Fig. 4(a)), the piezoelectric material is polarized electrically upon the application of external stress (or strain). By sandwiching this material between two electrodes, charges can be stored and delivered to an external load producing electrical signals. From the linear theory of piezoelectricity (Covaci and Gontean, 2020; Priya *et al.*, 2017), the generated piezoelectric charges depend on the level of stress applied to the piezoelectric material, T :

$$P_{piezo} = d \times T \quad (5)$$

where P_{piezo} is the vector of piezoelectric polarization, and d is the piezoelectric coefficient. Polarization causes the generation of the internal electric field, E_{piezo} , which relates to the elastic property of the material as follows:

$$E_{piezo} = \frac{P_{piezo}}{\epsilon} = \frac{d \times T}{\epsilon} = \frac{d \times (c \times S)}{\epsilon} = \frac{e \times S}{\epsilon} \quad (6)$$

where c is the elastic constant, S is the applied strain, e is the piezoelectric stress constant, and ϵ is the dielectric permittivity of the piezoelectric material. In general, when a piezoelectric material is subjected to vertical or tensile force, the material is deformed as depicted in Fig. 4(a). Hence, Eq. (6) implies that a large amount of applied stress leads to a high electric field, leading to the piezoelectric charges generated near the surface of material.

For the indirect piezoelectric effect, the production of mechanical strain S is directly proportional to the magnitude of the applied electrical field E as:

$$S = d \times E \quad (7)$$

Also, the linear elastic material can be stated by Hooke's law:

$$S = s \times T \quad (8)$$

where s is the elastic compliance.

The external electric field applied causes storage of charges on electrodes (Fig. 4(b)), resulting in the internal strain of the piezoelectric material that will compress or expand in a poling direction, as described in Eq. (7). If the direction of the electric field is the same as that of the poling field, the resultant strain is positive, and the material elongates. In the reverse process, the strain is negative and the material undergoes compression. The electric displacement D can be expressed as:

$$D = \epsilon \times E \quad (9)$$

If the applied electric field is maintained constant, the internal polarization will increase the electric displacement D_{total} according to:

$$D_{total} = \epsilon \times E + P_{piezo} \quad (10)$$

From the linear theory, the tensors in strain-charge form are used to describe the coupling among mechanical strain, mechanical stress, electric field, polarization, dielectric variables, and electric displacement as follows (Ikeda, 1990; Priya *et al.*, 2017):

$$D_p = d_{pQ} T_Q + \epsilon_{pq}^T E_p \quad (\text{direct effect}) \quad (11)$$

$$S_p = s_{pQ}^E T_Q + d_{pp} E_p \quad (\text{indirect effect}) \quad (12)$$

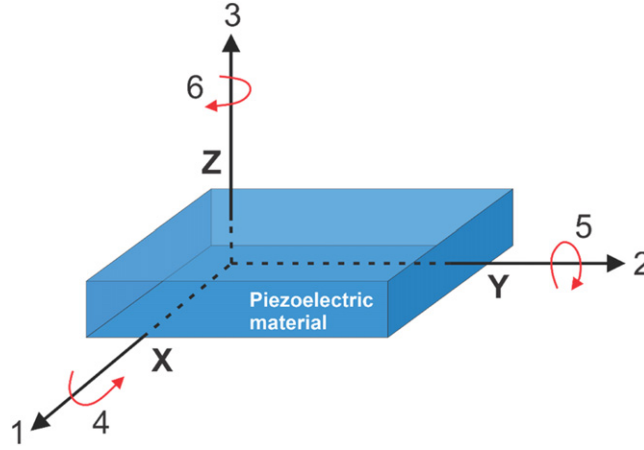


Fig. 6 Tensor directions of the piezoelectric effect.

where s_{pq}^E is an elastic compliance vector at a constant electric field, ϵ_{pq}^T is a dielectric permittivity tensor at constant stress, d_{pq} and d_{pp} are direct piezoelectric coefficient tensors, T_Q is a mechanical stress in Q direction, E_p is an electric field in p direction, D_p is a linear electric displacement in p direction, and S_p is a mechanical strain in P direction. It should be noted that the external force can be applied in diverse directions as well. In general, three Cartesian coordinate systems, *i.e.*, X , Y and Z , are used to identify the possible direction applied to the piezoelectric materials (Priya *et al.*, 2017). As explained previously in Fig. 4(a), the applied force can be vertical, horizontal, and shear. Accordingly, the notations 1, 2 and 3 describe the general directions applied directly along the X , Y and Z axes, respectively (Fig. 6). The corresponding shear forces are represented as 4, 5 and 6 along X , Y and Z axes, respectively. Consequently, as explained in Eqs. (11) and (12), the subscriptions, p and q , are indexed in 1–3 directions, and P and Q can be in 1–6. Moreover, D and E are 3×1 tensors, relating to the three main coordinated systems: X , Y and Z . In addition, S and T are 6×1 tensors, describing the vertical stress (or strain) (index: 1–3), and shear stress (or strain) (index: 4–6). The expanded matrix forms of Eqs. (11) and (12) can be written as (Ikeda, 1990):

$$\begin{bmatrix} D_1 \\ D_2 \\ D_3 \end{bmatrix}_{3 \times 1} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix}_{3 \times 6} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix}_{6 \times 1} + \begin{bmatrix} \epsilon_{11}^T & \epsilon_{12}^T & \epsilon_{13}^T \\ \epsilon_{21}^T & \epsilon_{22}^T & \epsilon_{23}^T \\ \epsilon_{31}^T & \epsilon_{32}^T & \epsilon_{33}^T \end{bmatrix}_{3 \times 3} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix}_{3 \times 1} \quad (\text{Direct effect}) \quad (13)$$

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix}_{6 \times 1} = \begin{bmatrix} s_{11}^E & s_{12}^E & s_{13}^E & s_{14}^E & s_{15}^E & s_{16}^E \\ s_{21}^E & s_{22}^E & s_{23}^E & s_{24}^E & s_{25}^E & s_{26}^E \\ s_{31}^E & s_{32}^E & s_{33}^E & s_{34}^E & s_{35}^E & s_{36}^E \\ s_{41}^E & s_{42}^E & s_{43}^E & s_{44}^E & s_{45}^E & s_{46}^E \\ s_{51}^E & s_{52}^E & s_{53}^E & s_{54}^E & s_{55}^E & s_{56}^E \\ s_{61}^E & s_{62}^E & s_{63}^E & s_{64}^E & s_{65}^E & s_{66}^E \end{bmatrix}_{6 \times 6} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix}_{6 \times 1} + \begin{bmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \\ d_{41} & d_{42} & d_{43} \\ d_{51} & d_{52} & d_{53} \\ d_{61} & d_{62} & d_{63} \end{bmatrix}_{6 \times 3} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix}_{3 \times 1} \quad (\text{Indirect effect}) \quad (14)$$

Figures of Merit for Piezoelectric Energy Harvesting

Piezoelectric energy harvesting requires a standard that quantifies harvesting performance. Figures of merit (FOM) for piezoelectric energy harvesting, including piezoelectric strain constant d , piezoelectric voltage coefficient g , electromechanical coupling factor k , electrical quality factor Q_e , mechanical quality factor Q_m , and acoustic impedance Z_a , is essential tool that has been used widely for piezoelectric device development (Uchino, 2017; Jaffe, 1971).

The first factor for FOM is d , which has the same meaning as the piezoelectric coefficient shown in Eq. (7). This factor is highly essential for actuator design and application. Next, for a direct effect suitable for harvesting and sensing applications, g is considered in terms of the generated electric field. The relation is shown in Eq. (6), where g corresponds to $d/\epsilon = d/(\epsilon_0 \cdot \epsilon_r)$ and ϵ_r is the relative dielectric permittivity. Another important factor for FOM is k . It is defined in terms of the ratio between the production of electrical energy U_{PE} and input mechanical energy U_{IM} for the direct effect, and the reverse for the indirect effect (Uchino, 2017).

$$k^2 = \frac{\text{electrical energy converted from Mechanical energy}}{\text{Input mechanical energy}} = \frac{U_{PE}}{U_{IM}} \quad (\text{Direct effect}) \quad (15)$$

or

$$k^2 = \frac{\text{mechanical energy converted from Electrical energy}}{\text{Input electrical energy}} = \frac{U_{PM}}{U_{IE}} \quad (\text{Indirect effect}) \quad (16)$$

The value of k^2 is < 1 , thus k is < 1 for the conversion of mechanical to electrical energy. Different piezoelectric materials exhibit different values of k . For example, the values of k are 0.1 for quartz, 0.4 for barium titanate (BaTiO_3 ; BT) ceramic, 0.5–0.7 for $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ceramic, and 0.9 for Rochelle salt recorded at 24°C (Jaffe, 1971).

The fourth factor is Q_e , the charge leakage of a piezoelectric sample (Uchino, 2017):

$$Q_e = \frac{1}{\tan\delta} \quad (17)$$

where $\tan\delta$ is the tangent or dielectric loss of the piezoelectric material. Next, Q_m is defined as the ratio of stored mechanical energy and the dissipated power, P_d , by elastic mechanisms of a piezoelectric material (Shekhani and Uchino, 2014):

$$Q_m = 2\pi f \frac{U_{PM}}{P_d} \quad (18)$$

It is found that Q_m can quantify the performance of a piezoelectric resonator by characterizing the feature of fundamental resonance. Let us assume that the equivalent circuit of a piezoelectric system consists of resistance, inductance and capacitance. Then, R_e , L_e and C_e are in series configuration but in parallel with the internal capacitance C_0 (Anon, 1988). Accordingly, Q_m is defined as (Amarande et al., 2007; Anon, 1988):

$$Q_m = \frac{\sqrt{L_e/C_e}}{R_e} = \frac{f_m f_n \sqrt{R_{max} G_{max}}}{f_n^2 - f_m^2} = \frac{f_n^2}{2\pi Z_m (C_0 + C_e) (f_n^2 - f_m^2)} \quad (19)$$

with the relationships:

$$R_e = \frac{1}{G_{max}}, L_e = \frac{1}{4\pi^2 f_m^2 C_e}, C_e = C_0 \frac{f_n^2 - f_m^2}{f_m^2}, \quad \text{and} \quad C_0 = \frac{1}{2\pi f_n} \sqrt{\frac{G_{max}}{R_{max}}}$$

where f_m and f_n are frequencies at maximum and minimum admittances, respectively, which correspond to maximum conductance G_{max} and resistance R_{max} , and Z_m is the minimum impedance of the material at the resonance point.

Acoustic impedance Z_a is used to evaluate the acoustic energy transfer of piezoelectric materials. The definition is (Uchino, 2017; Bui et al., 1988):

$$Z_a^2 = \frac{\text{Produced pressure}}{\text{Volume velocity}} \quad (20)$$

and for solid material:

$$Z_a = \sqrt{\rho_p v} \quad (21)$$

where ρ_p is density, and v is an acoustic velocity of the material.

PENG Modeling

To effectively design PENG for energy harvesting and sensing, mode of the device structure and electrical output performance are crucial. There are various points that should be considered, including working modes, material property, input and output relations, and an equivalent circuit model (Covaci and Gontean, 2020).

As depicted in Fig. 3(a) and Fig. 6, the working modes of PENG comprise of vertical compression and tension (transverse or 33 mode), horizontal compression and tension (longitudinal or 31 mode), and shear forces. PENG structure generally consists of several layers of the active piezoelectric material sandwiched between two electrodes. When an external strain is applied to the device, electrical signals are generated. The transverse mode of PENG is widely utilized for harvesters/sensors (Charoonsuk et al., 2019; Sriphan et al., 2021; Manchi et al., 2021), while the longitudinal mode suits unimorph and bimorph transducers (Wang et al., 2020; Jemai et al., 2015; Ali et al., 2019). Lastly, shear mode can be utilized typically for sensors (Kim et al., 2017; Williams et al., 2016).

The electricity generation of PENG depends on several factors of the box model as shown in Fig. 7. The input is external forces generating stress or strain to the piezoelectric energy collector. The output is electrical signals that are voltage and current. However, various performance variables are known to affect the harvesting/sensing performance, i.e., electric field, polarization, applied strain, thickness and area of the device, piezoelectric coefficient, and dielectric characteristics (Covaci and Gontean, 2020). These factors are essential for designing piezoelectric-based energy harvesters.

Without resonance, i.e., low frequency operation, the output voltage V is dominated mainly by the piezoelectric voltage coefficient, applied force F , the thickness of piezoelectric specimen l and active area A (Priya, 2010; Zhao et al., 2019):

$$V = El = -gTl = -\frac{gFl}{A} \quad (22)$$

According to Eq. (22), g is influenced largely by the output performance of the PENG, except for general factors. At low frequency, PENG configuration behaves like a parallel plate capacitor C . The energy produced is:

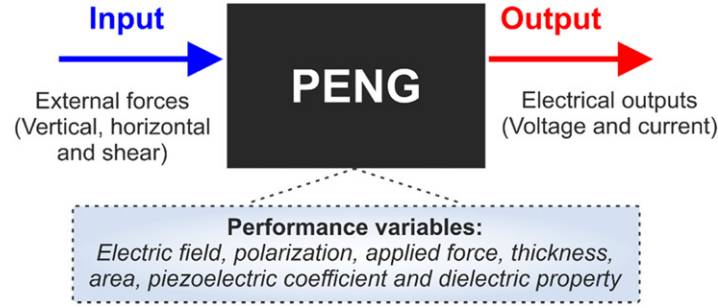


Fig. 7 Operation box of the PENG.

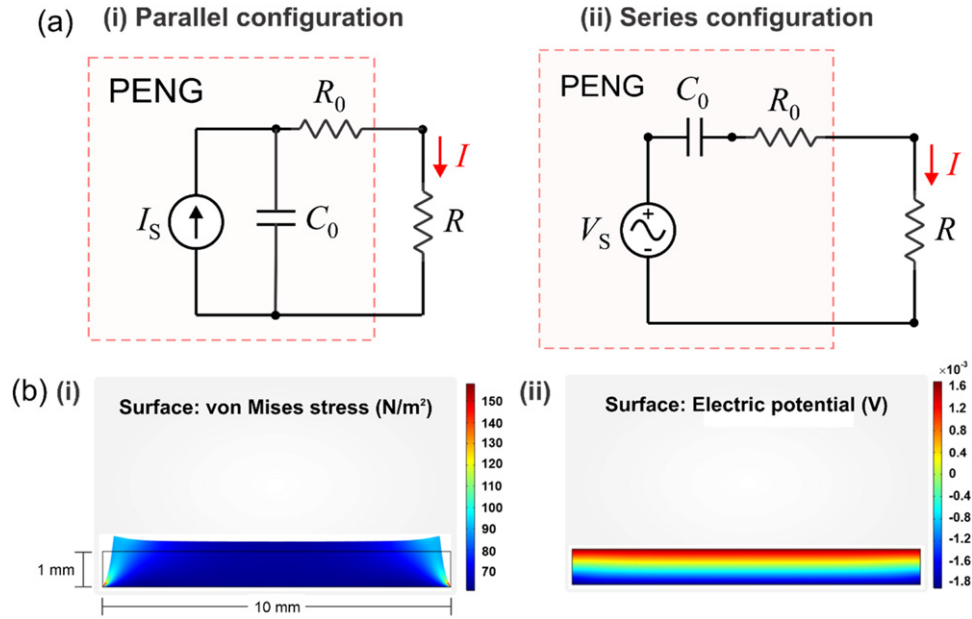


Fig. 8 (a) Equivalent circuit of PENG, and (b) FEM simulation for voltage production of PZT ceramic when subjected to vertical force.

$$U_{PE} = \frac{1}{2} CV^2 \quad (23)$$

and the energy conversion efficiency η is (Richards *et al.*, 2004):

$$\eta = \frac{1}{2} \left[\left(\frac{k^2}{1-k^2} \right) / \left(\frac{1}{Q_m} + \frac{1}{2} \frac{k^2}{1-k^2} \right) \right] \quad (24)$$

When polarization density is dependent on time t , the polarization current density, J_p , is defined by the following equation (Griffiths, 1999):

$$J_p = \frac{\partial P_{piezo}}{\partial t} = d \frac{\partial T}{\partial t} = e \frac{\partial S}{\partial t} \quad (25)$$

Eqs. (22)-(25) emphasize the role of improving piezoelectric charge production, which can finally boost PENG performance, by selecting a material containing high piezoelectric property and by applying high levels of stress and strain to the device.

In general, the piezoelectric sample used for the PENG is in a parallel plate configuration, as depicted in Fig. 8. In this case, the applied vertical strain in direction-3 (S_3) is dominant, and the strains in direction-1 and direction-2 (S_1 and S_2) are negligible:

$$S_3 = \frac{\Delta l}{l}, \quad S_1 = S_2 = 0 \quad (26)$$

From Eqs. (11) and (12), the following equations were obtained by considering the area:

$$A \bullet D_3 = A \bullet d_{33} T_3 + A \bullet e_{33}^T E_3 \quad (\text{Direct effect}) \quad (27)$$

$$A \bullet S_3 = A \bullet e_{33}^E T_3 + A \bullet d_{33} E_3 \quad (\text{Indirect effect}) \quad (28)$$

From Eqs. (6), (22) and (26), the following relations are obtained:

$$A \bullet D_3 = A \bullet d_{33} c S_3 + A \bullet e_{33}^T E_3 = A \bullet d_{33} \frac{c \Delta l}{l} + A \bullet e_{33}^T \frac{V}{l} \quad (29)$$

$$A \bullet \frac{T_3}{c} = A \bullet s_{33}^E c S_3 + A \bullet d_{33} E_3 = A \bullet s_{33}^E \frac{c \Delta l}{l} + A \bullet d_{33} \frac{V}{l} \quad (30)$$

or they can be written in terms of charges Q and forces F_a produced as follows (Anon, 1988):

$$Q = -c \alpha \Delta l + C_0 V \quad (31)$$

$$F_a = c^2 K_p^E \Delta l + c \alpha V \quad (32)$$

By differentiating Q with respect to time, the output current I can be obtained:

$$I = c \alpha \dot{\Delta l} - C_0 \dot{V} \quad (33)$$

$$F_a = c^2 K_p^E \Delta l + c \alpha V \quad (34)$$

Eqs. (29)–(34) are expressed through these relationships (Anon, 1988)

$$Q = AD, \alpha = -\frac{Ad_{33}}{l}, C_0 = \frac{Ae_{33}^T}{l}, F_a = AT, \text{ and } K_p^E = \frac{As_{33}^E}{l}$$

It is evident that the generated current from Eq. (33) relies on two terms. Firstly, the term $c \alpha \dot{\Delta l}$ relates to the mechanical movement and frequency of strain applied to piezoelectric material. Secondly, the term $C_0 \dot{V}$ focuses on the accumulated charges upon variation of electric potential across the piezoelectric sample. Under this circumstance, the equivalent circuit of the PENG is obtained by containing the current source in parallel with the internal capacitor (Fig. 8(a)-i), or voltage source and capacitor in series configuration (Fig. 8(a)-ii) (Xu and Qin, 2017; Kuang and Zhu, 2019). The charge generation term, $c \alpha \dot{\Delta l}$, can produce the source current, I_s . This current varies in AC form with respect to the change of voltage across C_0 during deformation (Fig. 4(a)-i). In a more complex case, the internal resistance, R_0 , can be combined with capacitor impedance for considering the contact resistance effect between the metal electrode and piezoelectric material, similar to the series resistance effect in the equivalent circuit model of a solar cell (Muhammadsharif et al., 2017; Prasatsap et al., 2020).

The finite element method (FEM) has been successfully used to simulate the behavior and output generation of PENG and conventional piezoelectric-based energy harvester (Jeong et al., 2018; Kim et al., 2018c; Ghosh and Mandal, 2016; Kuang and Zhu, 2019; Tian et al., 2018). FEM is a useful tool that enables the investigation of diverse theoretical parameters on physical outputs to verify the experimental results. For example, the application of FEM to simulate the voltage output of Pb(Zr,Ti)O₃ (PZT) – 5A ceramics, when subjected to external force, is shown in Fig. 8(b). With set conditions of 10 mm² of size and 100 N · m⁻² of applied force (Fig. 8(b)-i), the PZT specimen can generate the output voltage at mV level (Fig. 8(b)-ii), which is similar to that from the cantilever-structured piezoelectric harvester considered for the same size (Tian et al., 2018; Butt and Pasha, 2016).

Piezoelectric Materials for Energy Harvesting

1st generation: Piezoelectric Oxide Nanostructure

Since the first report of PENG by Wang et al. in 2006 (Wang and Song, 2006), the rapid development of energy harvesting and sensing technologies has expanded (Fig. 3). The first PENG structure consisted of well-aligned piezoelectric oxide nanostructures, i.e., zinc oxide nanowires (ZnO NWs) grown on a rigid α -Al₂O₃ substrate in [0001] direction. Owing to piezoelectricity, a single NW produces the voltage of ~6–9 mV as tested by a Si atomic force microscope (AFM) tip coated with Pt. In this example, zinc oxide with a Wurtzite crystal structure creates a strain field because of the lack of center of symmetry. The tetrahedrally coordinated Zn²⁺ and O²⁻ are stacked layer by layer along the threefold c -axis (Djurišić et al., 2012). This results in the separation of charged centers of cations and anions, and the production of induced piezoelectric potential across NWs under the applied external strain (Wang and Song, 2006). Accordingly, ZnO NWs have become the material of choice for developing piezoelectric-based devices in the first stage (Wang and Song, 2006; Shin et al., 2014; Choi et al., 2009; Chang et al., 2014; Hsu and Chen, 2012). Subsequently, other ZnO nanostructures such as nanorods (NRs) (Choi et al., 2009), nanobelts (Zhang et al., 2015b), and nanosheets (NSs) (Aminullah et al., 2020), have also been explored. As shown in Fig. 9(a), Choi et al. (2009) prepared a flexible PENG composed of ZnO NRs array deposited on a flexible indium tin oxide (ITO)-coated polyether sulfone (PES) substrate. With an area size of 9 cm², the transparent nanogenerator could generate an output current density reaching ~1 μ A · cm⁻² under the applied load of 0.9 kgf, which is sufficient for use as self-powered sensors. Besides ZnO-based nanomaterials, other piezoelectric materials can also be used for energy harvesting. An example by Wu et al. (2012) is presented in Fig. 9(b). They synthesized ZnSnO₃ microbelts (MBs) using a vapor transfer process. Individual ZnSnO₃ MB was used for piezoelectric energy conversion, producing electrical outputs of ~110 mV and ~80 nA for voltage and current, respectively, and demonstrate good stability with an increased operating frequency. In another example based on the outstanding piezoelectric property of PZT, Kim et al. (2008) reported ultra-thin-walled PZT nanotubes (NTs) with high remnant polarization and coercive field of ~1.5 μ C · cm⁻² and ~86 kV · cm⁻¹, respectively, under an applied electric field of 400 kV · cm⁻¹ (Fig. 9(c)). Scanning transmission electron microscopy (STEM) combined with energy dispersive X-ray spectroscopy (EDS) clearly confirmed the chemical

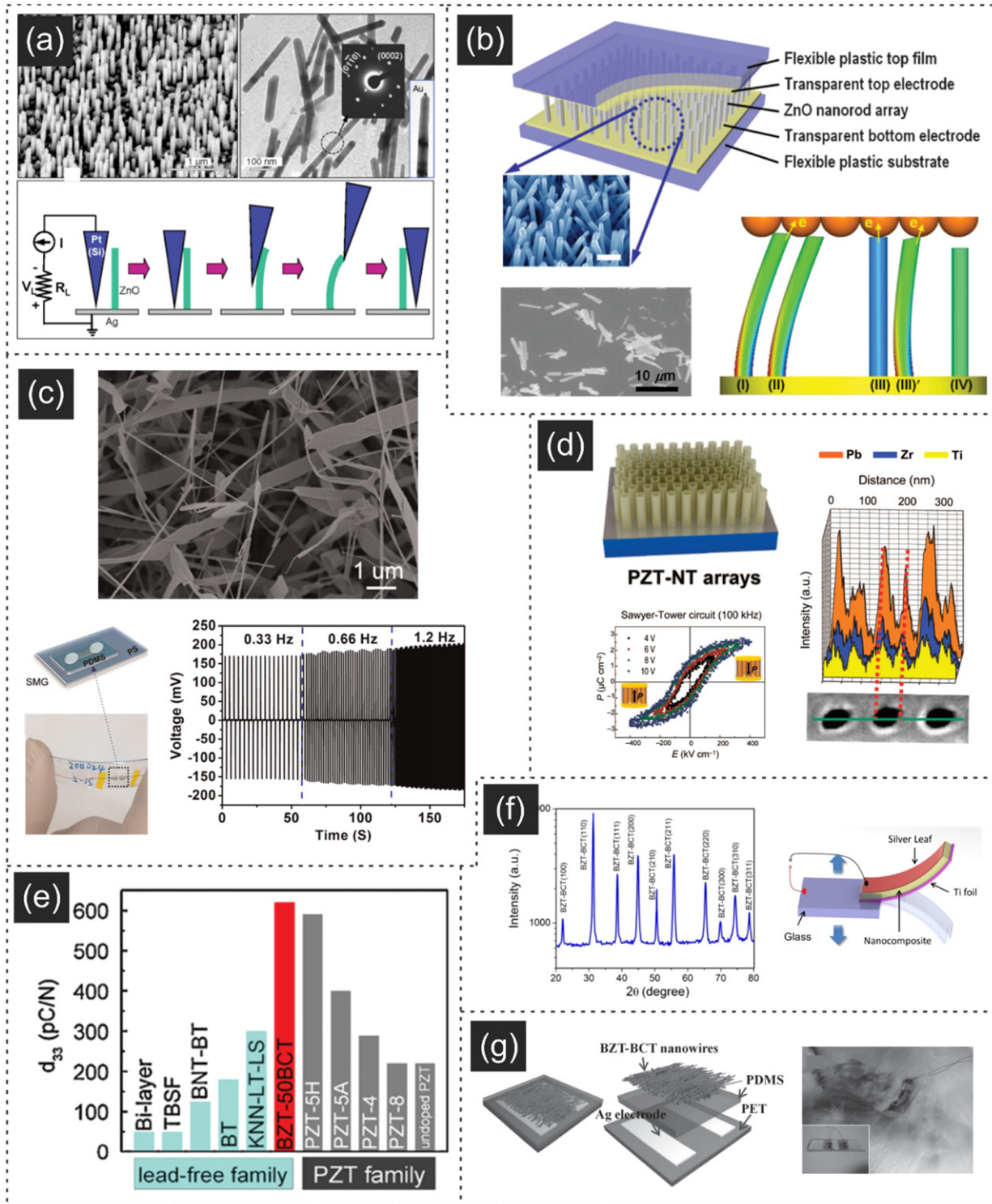


Fig. 9 (a) PENG structure containing aligned ZnO NRs array, FE-SEM image, and behaviors of different NRs under the applied external forces, (b) FE-SEM and crystallographic structure of ZnSnO₃ MBs, including a schematic diagram representing a single ZnSnO₃ MBs nanogenerator, and generated output voltage of ZnSnO₃ MBs PENG in various frequencies, (c) Illustration of PZT NTs array, STEM image, EDS line profile, and P - E hysteresis loops of PZT NTs grown on platinized silicon substrate, (d) Comparison of the d_{33} of BZT – 50BCT system with other non-Pb piezoelectric materials and PZT family, (e) XRD pattern of BZT-BCT NWs, structural configuration of the BZT-BCT NWs/PDMS PENG, and (f) Schematic diagram of the BZT-BCT NWs/PDMS PENG, and *in vivo* demonstration of the nanogenerator implanted into the back of a rabbit. Reproduced from Choi, M.-Y., Choi, D., Jin, M.-J., *et al.*, 2009. Mechanically powered transparent flexible charge-generating nanodevices with piezoelectric ZnO nanorods. *Adv. Mater.* 21, 2185–2189. Wu, J.M., Xu, C., Zhang, Y., Wang, Z.L., 2012. Lead-free nanogenerator made from single ZnSnO₃ microbelt. *ACS Nano* 6, 4335–4340. Kim, J., Yang, S. A., Choi, Y.C., *et al.*, 2008. Ferroelectricity in highly ordered arrays of ultra-thin-walled Pb(Zr,Ti)O₃ nanotubes composed of nanometer-sized perovskite crystallites. *Nano Lett.* 8, 1813–1818. Liu, W., Ren, X., 2009. Large piezoelectric effect in Pb-free ceramics. *Phys. Rev. Lett.* 103, 257602. Zhou, Z., Bowland, C.C., Malakooti, M.H., *et al.*, 2016a. Lead-free 0.5Ba(Zr_{0.2}Ti_{0.8})O₃–0.5(Ba_{0.7}Ca_{0.3})TiO₃ nanowires for energy harvesting. *Nanoscale* 8, 5098–5105. Yuan, M., Cheng, L., Xu, Q., *et al.*, 2014. Biocompatible nanogenerators through high piezoelectric coefficient 0.5Ba(Zr_{0.2}Ti_{0.8})O₃–0.5(Ba_{0.7}Ca_{0.3})TiO₃ nanowires for *in-vivo* applications. *Adv. Mater.* 26, 7432–7437.

composition of the PZT NTs. However, due to the toxicity of lead, which obstructs sustainable applications, the search for lead-free piezoelectric oxide materials with piezoelectric property close to PZT is highly essential. Non-Pb piezoelectric materials generally have lower piezoelectric property than the PZT family ($d_{33} < 300 \text{ pC} \cdot \text{N}^{-1}$). Emergence of the $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ - $(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BZT-BCT) system, which shows high d_{33} of $\sim 620 \text{ pC} \cdot \text{N}^{-1}$ has gained attention worldwide (Fig. 9(d)). The high d_{33} is because this composition locates near the critical point of the cubic-rhombohedral-tetragonal morphotropic phase boundary (Liu and Ren, 2009). Due to its excellent property, Zhou *et al.* (2016a) used the BZT-BCT system to harvest mechanical energy. They prepared large-scale BZT-BCT NWs based on a two-step hydrothermal reaction. The X-ray diffraction (XRD) pattern confirmed a pure perovskite-type tetragonal structure of BZT-BCT samples (Fig. 9(e)). Then, the BZT-BCT NWs were used to fabricate a flexible piezoelectric cantilever. Maximum peak-to-peak voltage and current results were $\sim 6.8 \text{ V}$ and $\sim 19 \text{ nA}$, respectively, when the cantilever vibrated at the maximum strain. Furthermore, the BZT-BCT-based PENG can be utilized for *in vivo* applications. As demonstrated by Yuan *et al.* (2014), the BZT-BCT NWs were packed inside biocompatible polydimethylsiloxane (PDMS) before embedding into the body of a rabbit (Fig. 9(f)). This device could be driven inside the body of a slow-walking rabbit to generate an output current of approximately 0.1 nA , without damage to the tissue. Hence, using the BZT-BCT NWs PENG has great potential for biomedical applications.

2nd Generation: Synthetic Piezoelectric Polymer and Composite

Piezoelectric ceramics such as BaTiO_3 , PbZrO_3 and ZnO , possess high dielectric and piezoelectric properties, *i.e.*, high piezoelectric coefficient, high pyroelectric constant and strong electromechanical coupling. However, they are brittle and inflexible, such that their direct use in flexible electronics is difficult. On the other hand, polymers are easy to process into thin films, and have low density and high breakdown strength. Some polymers of interest for piezoelectric energy harvesting include poly(vinylidene fluoride) (PVDF) that incorporates other monomers, and Nylon-11. While these polymers usually have a lower piezoelectric coefficient than their ceramic counterparts, they can be applied as a matrix containing ceramic fillers with enhanced performances.

PVDF

PVDF has a general formula $(\text{CH}_2\text{CF}_2)_n$ and exists in five structures (α , β , γ , δ , ϵ) that vary in configuration of the hydrofluorocarbon chain from fully-trans (T) to gauge (G). The β - and γ -phase appear to be the most electrically active and are employed widely for energy harvesters. The β -phase can be obtained by mechanical stretching (drawing) or electric poling. Its properties and applications have been reviewed thoroughly by several authors (Ruan *et al.*, 2018; Chen *et al.*, 2017a; Wan and Bowen, 2017).

In a pioneer work, Chamankar *et al.* (2020) demonstrated that mechanical stretching and electric poling occurred simultaneously *via* electrospinning, thus yielding PVDF mostly in the β -phase. The authors dissolved PVDF in a mixture of dimethyl-formamide/acetone and mixed it with PZT particles. The mixture was sonicated and electrospun at a voltage of 20 kV . It was found that the PZT filler increases the size of the fibers, with 37 vol% PZT leading to a fiber with a diameter of 340 nm (Fig. 10(a)). The increased filler content is accompanied by the increasing relative proportion of the polar β -phase, the increasing dielectric constant, and the increasing figure of merit, as shown in Fig. 10(b) - (d). The generated output voltage of 37 vol% PZT-PVDF was $\sim 184 \text{ mV}$ under an applied force of $\sim 2 \text{ N}$, with piezoelectric sensitivity of $\sim 174 \text{ mV} \cdot \text{N}^{-1} \cdot \mu\text{m}^{-1}$. This presents a significant increase from PVDF alone.

In another highly-cited work, Jana *et al.* (2015) reported selective formation of the polar β -phase of PVDF by adding up to 2.0 wt% of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. While the Mg-free film was mostly α -phase, the one with 2.0 wt% filler had a predominating (90%) β -phase. This was deduced from characteristic IR vibrations and XRD patterns in combination with SEM observations. The enhanced piezo-response was due to the combined effect of the β -phase and the hydrogen bonding between Mg-salt and PVDF. The stronger polarity of the hydroxyl groups was evident from the broad and increasing intensity of the band at 3380 cm^{-1} typically ascribed to O-H stretching in the IR spectrum. This was accompanied by an increasing dielectric constant and AC conductivity. It was notable that the nanogenerator delivered up to 4 V open circuit voltage by simply repeating human finger imparting.

The composites also can be prepared as a simple laminate. Vatansever *et al.* (2011) investigated the voltage responses of ceramic/piezoelectric fiber composite and polymer based piezoelectric strips. The authors studied the effect of wind speeds and water droplets, including material dimensions and drop mass, by releasing water drops from a height and wind from a wind tunnel. It was found that the voltage generated for a shorter PVDF sample was higher in the water drop experiment. This was due to the faster reaction of the shorter film to the forward strain. Meanwhile, the voltage generated by a longer PVDF film was higher in the wind tunnel experiment, because the wind exerted a larger force onto the larger surface area of the film.

Copolymer of PVDF

The β -phase of PVDF also can be promoted when a copolymer is incorporated into PVDF, most commonly trifluoroethylene (TrFE), hexafluoropropylene (HEP), and chlorotrifluoroethylene (CTFE) (Liu *et al.*, 2016b; Wan and Bowen, 2017). For PVDF-TrFE, the nonpolar phase has the lowest energy according to density functional theory (DFT) calculations. The fluorine atoms in the TrFE ($-\text{CHF}-\text{CF}_2-$) comonomer unit force the polymer chains to align in an extended planar zigzag trans (T) form, leading to higher crystallinity and polar β -phase of PVDF-TrFE. PVDF-TrFE, with 30 mol% TrFE, exhibited ferroelectric transition above room temperature, with a large thermal hysteresis. Extensive measurements by Legrand (1989) indicated both small crystallites and

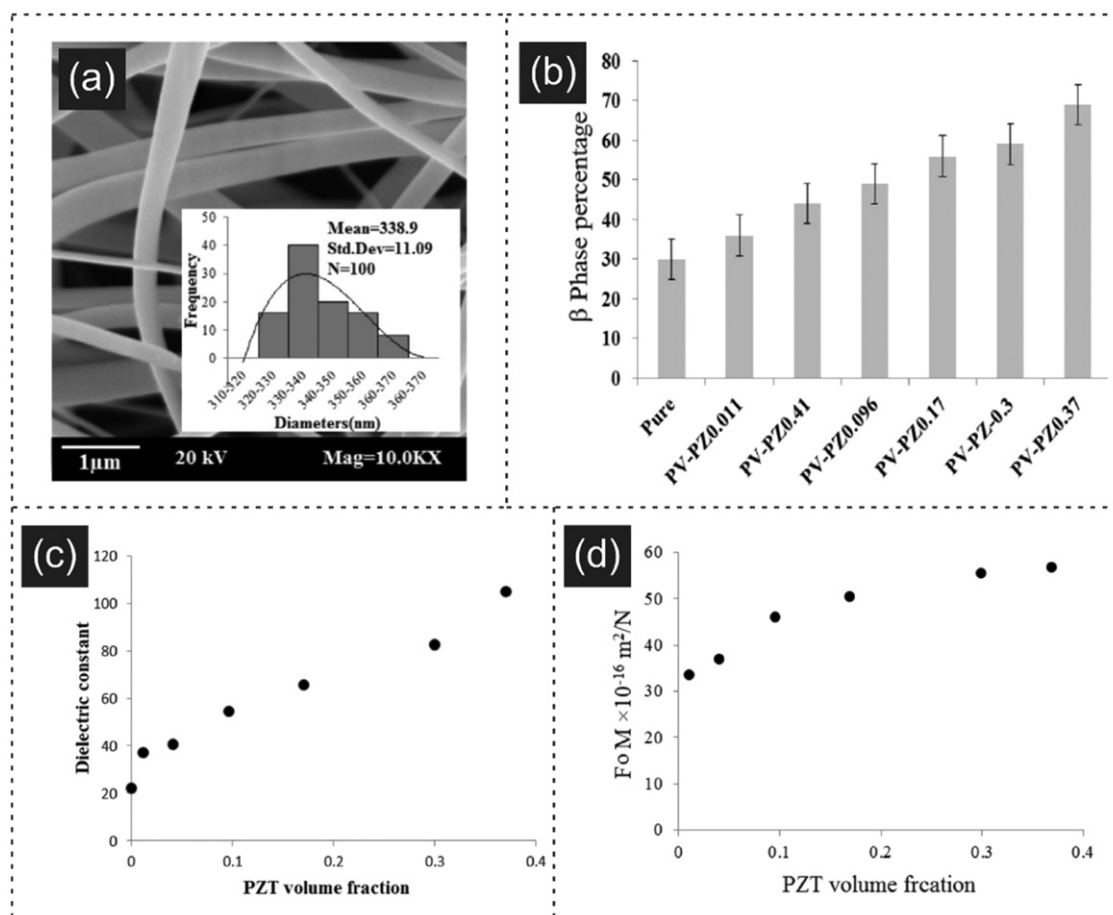


Fig. 10 (a) SEM image of PVDF with 37 vol% PZT. The dependence of (b) β -phase of PVDF, (c) dielectric constant, and (d) figure of merit of the composite as a function of the PZT volume fraction. Reproduced from Chamankar, N., Khajavi, R., Yousefi, A.A., et al., 2020. A flexible piezoelectric pressure sensor based on PVDF nanocomposite fibers doped with PZT particles for energy harvesting applications. *Ceram. Int.* 46, 19669–19681.

amorphous inter-crystalline regions. In addition, temperature cycling effectively modifies the superstructure to enhance the degree of crystallinity of the polymer. Regarding PVDF-co-HFP, the bulky $-\text{CF}_3$ of HFP provides more space to allow dipoles to reorient.

In the pioneering work of Pi *et al.* (2014), PVDF-TrFE (25 mol% TrFE) powder was dissolved in diethyl carbonate prior to spin coating on polyimide substrate. This copolymer film was thermopoled at $0.5\text{--}0.8 \text{ MV} \cdot \text{cm}^{-1}$ and 100°C for 30 min, resulting in a nonpolar-to-polar α -to- β phase transition according to X-ray diffraction and IR spectroscopy. The device exhibited positive voltage and current pulses of 7 V and 58 nA, respectively, corresponding to the current density of $0.56 \text{ mA} \cdot \text{cm}^{-2}$. After repeated testing at 0.75 Hz for 1 h, a decrease of only 14% and 6.5% of open circuit voltage and short circuit current was observed, respectively, indicating good stability of the device.

The PVDF-copolymer can be modified further by compositing with dielectric inorganic fillers, making a multilayer, or fabricating into micro/nanostructures. A typical example is PVDF-TrFE/ZnO composite (Dodds *et al.*, 2012). Spin-coated film showed increasing remnant polarization with increasing ZnO content. At 20 wt% ZnO, the composite delivered $15.2 \text{ mC} \cdot \text{m}^{-2}$ compared to $5.8 \text{ mC} \cdot \text{m}^{-2}$ without ZnO. However, the breakdown voltage undesirably decreases with increasing ZnO. Graphene-PVDF-TrFE bilayers (Bae *et al.*, 2013) and graphene oxide-PVDF-TrFE bilayers (Bhavanasi *et al.*, 2016) have been prepared. Graphene-PVDF-TrFE bilayers with poling show resistance of $188 \Omega \cdot \text{sq}^{-1}$ while those of a sample without poling show $353 \Omega \cdot \text{sq}^{-1}$. This indicates the graphene adding on PVDF-TrFE is helpful in increasing electrical conductivity of the composite. Meanwhile, the graphene oxide-PVDF-TrFE bilayers show a voltage and power output of 4 V and $4.4 \text{ mW} \cdot \text{cm}^{-2}$, respectively, which is an improvement compared to poled PVDF-TrFE alone (1.9 V and $1.8 \text{ mW} \cdot \text{cm}^{-2}$). Other examples include the imprinted PVDF-TrFE/BaTiO₃ nanocomposite micropillars (Chen *et al.*, 2017b), or PVDF-TrFE nanotubes (Bhavanasi *et al.*, 2014), both of which showing superior output performances when compared to the films, indicating the beneficial effect of micro/nanostructures.

Nylon-11

Nylons are polyamide fibers. The even-numbered, nonferroelectric Nylon (*e.g.*, Nylon-6,6) has been used successfully in the textile industry as fabric. Even-numbered nylons pack in such a way that the dipoles associated with hydrogen bonds are canceled.

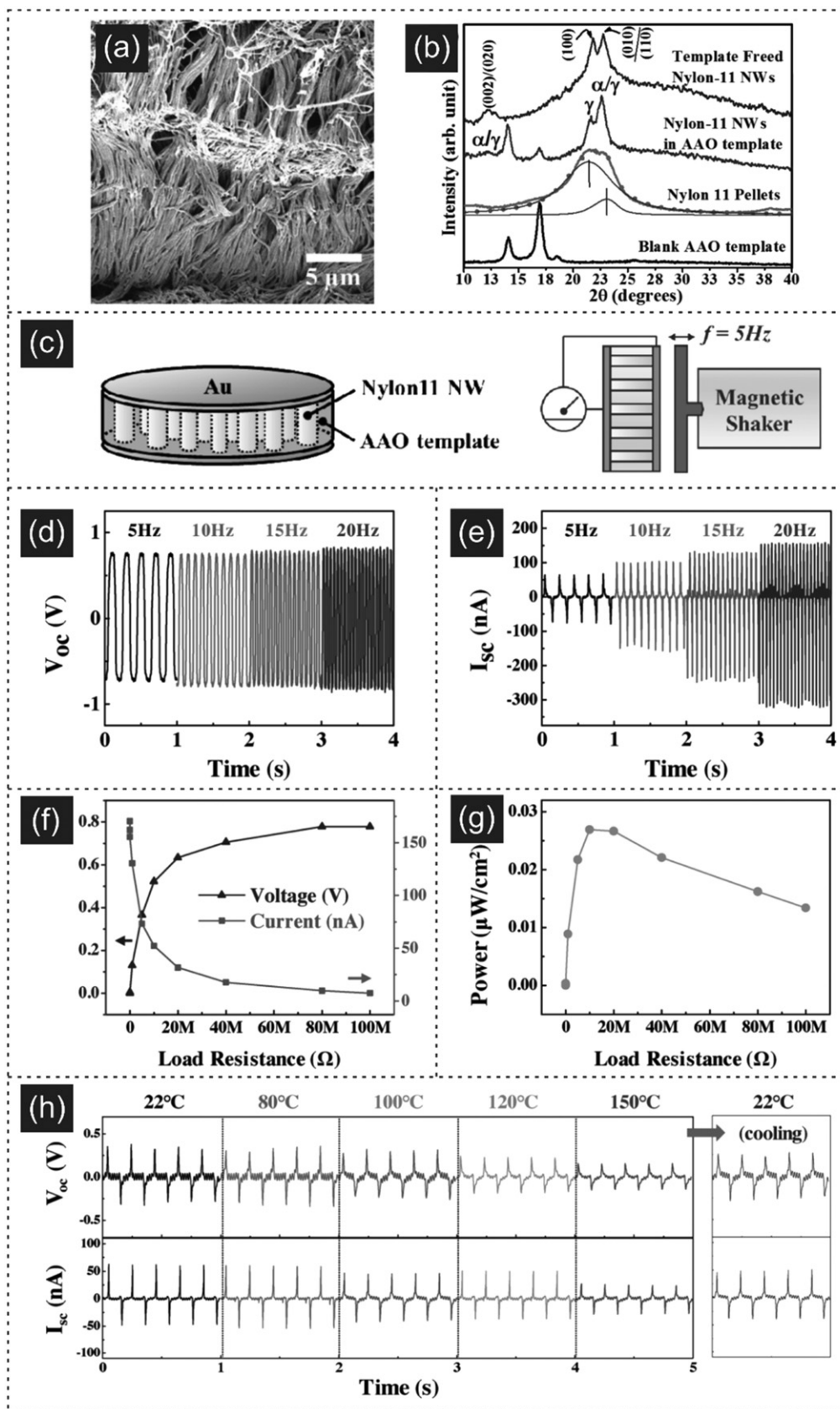


Fig. 11 (a) SEM image of Nylon-11 nanowires freed from the AAO template, (b) comparison of XRD patterns, (c) testing structure of the device, (d) V_{OC} , and (e) I_{SC} in response to periodic impact at different frequencies, (f) and (g) variation of voltage, current, and peak power density with load resistance, and (h) output performance from 22° to 150°C. Reproduced from Datta, A., Choi, Y.S., Chalmers, E., et al., 2017. Piezoelectric Nylon-11 nanowire arrays grown by template wetting for vibrational energy harvesting applications. *Adv. Funct. Mater.* 27, 1604262.

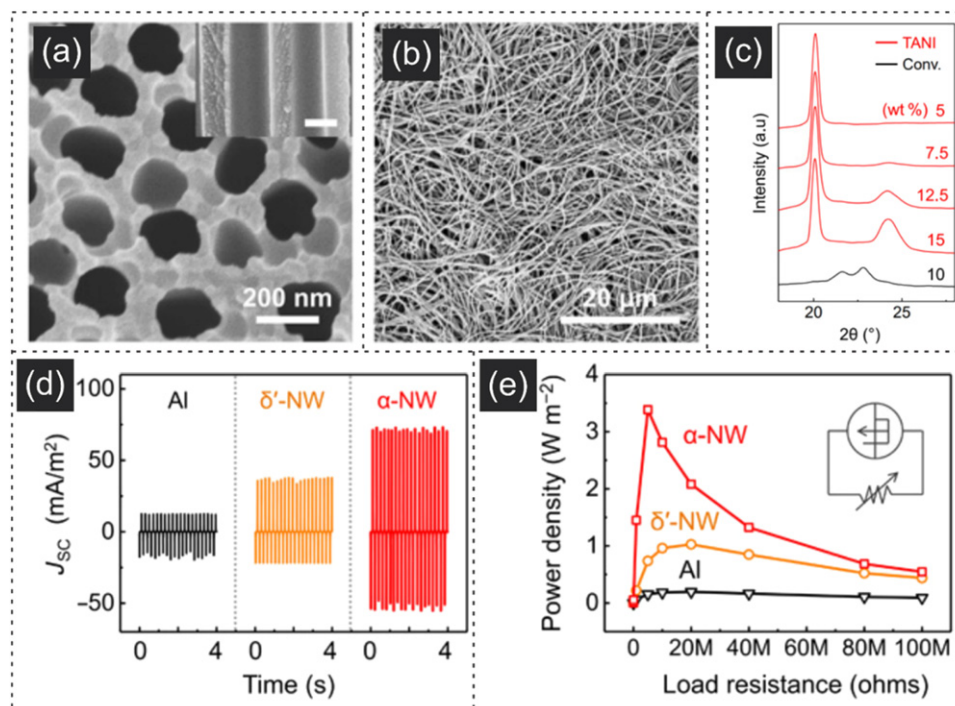


Fig. 12 (a) SEM image of the AAO template and cross section in the inset, (b) SEM image of the α -phase nylon-11 nanowires synthesized by the TANI method, (c) XRD patterns of nanowires from different concentrations of the precursor, including those from a conventional template-wetting method, (d) short-circuit current density of triboelectric nanogenerators with different materials, and (e) corresponding power densities (Choi Yeon *et al.*).

Meanwhile, odd-numbered, ferroelectric Nylon [Nylon-11, $(C_{11}H_{21}ON)_n$] has been utilized just very recently in energy harvesting applications. Odd-numbered nylons have at least three stable crystalline polymorphs, including triclinic α -phase, which is hydrogen-bonded strongly, and a piezoelectric pseudohexagonal γ -phase, among others.

In the pioneer work of Datta *et al.* (2017), the sample was prepared by a simple capillary wetting of Nylon-11 pellet solution in formic acid, inside an anodized aluminum oxide (AAO) template. The Nylon-11 nanowires had a diameter of 200 nm and length of up to 50 mm, representing a high aspect ratio, as shown in Fig. 11(a). Fig. 11(b) compares the XRD patterns of the samples at different stages. The synthesis leads to a mixture of α phase and γ phase, when compared to the initial/commercial pellet that lacks the long-range order. The varying ratio of the α -to- γ phase of Nylon 11, either inside or freed from the AAO template, suggests competition of these phases.

A device based on such vertically-aligned Nylon-11 nanowires was fabricated by gold sputtering on both sides of the template (Fig. 11(c)). The device was “self-poled”, *i.e.*, it did not require prior poling process. The mechanical impact was perpendicularly applied periodically to the long axis of the nanowires. Fig. 11(d) and (e) show the open-circuit voltage (V_{OC}) and short-circuit current (I_{SC}), which peak at approximately 1 V and 100 nA, respectively, from 5 to 20 Hz. By measuring the electrical output across different load resistances (Fig. 11(f)), a peak in output power density of $0.03 \text{ mW} \cdot \text{cm}^{-2}$ was observed up to 10 M Ω (Fig. 11(g)). In addition, successful operation at 150°C has been demonstrated, which might be suitable for use with vibrating car engines or heavy machinery. The output performance was almost fully recovered upon returning to room temperature (Fig. 11(h)). The high temperature operation of Nylon-11 presents a clear advantage compared to PVDF and its copolymers.

Tunability of the crystalline phase of Nylon-11 has become promising for the optimization of output performance. In yet another example, Choi *et al.* (Choi *et al.*, 2020) demonstrated the energy-harvesting performances of the sole α -phase nylon-11 (instead of a mixture of α -phase and γ phase). As mentioned above, tightly packed hydrogen bonds limit dipole rotation until electrical breakdown. Therefore, the α -phase is polar but considered non-ferroelectric. Here, the authors developed the “thermally assisted nanotemplate infiltration (TANI)” method to prepare nanowires. The AAO nanoporous template (Fig. 12(a)) was in contact with precursor vapor (dissolved in formic acid) instead of making direct contact. The authors obtained long chain-shaped nanowires with uniform width (200 nm) and length (60 mm), as shown in Fig. 12(b). This solvent-vapor filled closed-heating system of TANI mimics the slow crystallization typical for the α -phase. Fig. 12(c) shows the XRD patterns of the α -phase that indicate the strong (200)-reflection ($2\theta = 20^\circ$) at the optimized (5 wt%) concentration of the precursor. This is ascribed to the perpendicular orientation of the molecular chain relative to direction of the nanowire length. Otherwise, the conventional template-wetting method fails to provide the α -phase. Fig. 12(d) shows the short-circuit current density (J_{SC}) of the α -phase nanowire-based triboelectric generator of $\sim 74 \text{ mA} \cdot \text{m}^{-2}$, compared to ~ 38 and $\sim 13 \text{ mA} \cdot \text{m}^{-2}$ for the δ' - and Al-based devices, respectively. This corresponds to the peak output power densities of 3.38, 1.03, and $0.099 \text{ W} \cdot \text{m}^{-2}$, respectively, as shown in

Table 3 Comparison of piezoelectric constants for various organic piezoelectric biomaterials

Bio-piezoelectric materials	Piezoelectric property d_{33}
Virus	7.8 pC.N ⁻¹
Aligned phage nanopillars	10 pC.N ⁻¹
Silk fibroin	38 ± 2 pm.V ⁻¹
Cellulose nanofibril/PDMS	19 pC.N ⁻¹
γ- glycine	10 pC.N ⁻¹
Fish scale	5.5 pC.N ⁻¹
Fish bladder	22 pC.N ⁻¹
Eggshell membrane	23.7 pC.N ⁻¹
Human bone	7–8 pC.N ⁻¹
Poly (γ-benzyl α, L-glutamate)	25 pC.N ⁻¹

α-crystalline structure. The dipoles of PLLA are introduced normally by carbonyl (C=O) groups that are not aligned with the main chain. External stimuli can be applied to preferentially oriented dipoles in a stretched direction (Fig. 13(b)) (Sultana *et al.*, 2017). These unidirectionally-oriented dipoles are in the form of β-crystalline structure, resulting in shear piezoelectricity of $d_{14} = 12 \text{ pC} \cdot \text{N}^{-1}$ (Sultana *et al.*, 2017; Tajitsu, 2008). It is worth noting that β-crystalline PLLA can occur without a polling process. Excellent phase and amplitude responses from PLLA have been observed from −25 V to +25 V applied voltage through the AFM tip. Response of the piezoresponse force microscopy (PFM) phase demonstrates rectangular hysteresis *versus* voltage diagram (Fig. 13(d)). Hysteretic switching by 180° corresponds to switching direction of C=O dipole polarization. The PFM amplitude response is also hysteretic with the “butterfly loop”, as shown in Fig. 13(e). Each point of the butterfly loop implies piezoelectric deformation. The piezoelectric coefficient, d_{33} , can be estimated from the slope of amplitude *versus* voltage that is found to be $\sim 3 \pm 1 \text{ pm} \cdot \text{V}^{-1}$ (Sultana *et al.*, 2017).

Polysaccharide-based materials

Polysaccharides are carbohydrates comprised of multiple long-chain bonded sugar molecules. They are used in a wide variety of applications including mechanical, chemical and electrical fields. This session focuses particularly on polysaccharide polymers commonly used in energy harvesting applications, such as cellulose, chitin, chitosan and alginate.

Cellulose

Cellulose, the highly abundant natural polysaccharide, was isolated firstly from wood by Asselme Payan in 1838 (Rajinipriya *et al.*, 2018). As illustrated in Fig. 14(a), cellulose is a linear-chain of glucose monomers linked together as a repeat unit by a β-1,4-glucosidic bond, with each of them composed of three hydroxyl groups (Rajinipriya *et al.*, 2018). Strong hydrogen bonds of the hydroxyl groups, with a high degree of polymerization, allow cellulose to form highly crystalline structures. The cellulose molecules are organized in nanofibrils (5–50 nm) and aggregate to form microfibrils of several micrometers in diameter. The SEM image of cellulose with randomly oriented fibers is presented in Fig. 14(b) (Ratajczak and Stobiecka, 2020; Song *et al.*, 2021). Apart from several industrial applications *i.e.*, packaging, paper, wooden furniture, food, cosmetics, pharmaceutical products and clothes (Trache *et al.*, 2020), cellulose is being proposed as a promising source of electronic materials for energy storage, sensors and energy harvesting technologies.

In 1955, piezoelectricity of cellulose was first reported in wood cellulose fiber with a shear piezoelectric constant of $d_{25} = -d_{14}$, in the order of 10^{-9} , which was about 0.05 times that of the d_{11} of quartz (Fukada, 1955). The piezoelectricity originated from an orderly non-centrosymmetric arrangement of the polar hydroxyl group, where the net dipole moment is not zero. Cellulose crystals co-exist naturally in two polymorphs (Fig. 14(c)), I_α and I_β , with the latter being a more stable phase. Cellulose I_α stabilizes in a triclinic crystal structure. Meanwhile, cellulose I_β has a monoclinic $P2_1$ (#4) structure, which does not have a center of symmetry (Dri *et al.*, 2014). The chain structure and chain arrangement of cellulose I_β and its bonding leads to anisotropic properties including mechanical, electrical and thermodynamic properties. The three kinds of hydrogen-bond interactions between O2-H and O6, O3-H and O5, and O3-H and O6 in each cell show high piezoelectric responses of $36.4 \text{ pm} \cdot \text{V}^{-1}$, $10 \text{ pm} \cdot \text{V}^{-1}$ and $4.3 \text{ pm} \cdot \text{V}^{-1}$, respectively, according to DFT simulation (Moon *et al.*, 2011; Chae *et al.*, 2018). Molecular chains of cellulose are linked with the hydrogen bond inter-chain along the (110)_i and (200)_m planes to form coexisting hydrogen bonding networks (Moon *et al.*, 2011). This causes polar hydrogen bonds to become a net dipole in a non-centrosymmetric order and shows piezoelectric activity (Fig. 14(d)). However, the piezoelectric constant of cellulose is very low. It is reported that d_{33} of cellulose is $0.4 \text{ pC} \cdot \text{N}^{-1}$ (Dri *et al.*, 2014), which is far from that of the synthetic piezoelectric polymer PVDF ($d_{33} = 21 \text{ pC} \cdot \text{N}^{-1}$). In recent years, works have mainly focused on advanced technology for improving piezoelectric properties of cellulose by adding piezoelectric filler. For example, adding BT nanoparticles by 48 wt% into the lignocellulose matrix could improve longitudinal d_{33} to $4.8 \text{ pC} \cdot \text{N}^{-1}$ (Mahadeva *et al.*, 2014). Similarly, adding 27 wt% MnFe_2O_4 nanoparticles could improve d_{33} of cellulose significantly to 20–23 $\text{pC} \cdot \text{N}^{-1}$, which is close to that of commercial PVDF polymer (Sriplai *et al.*, 2020).

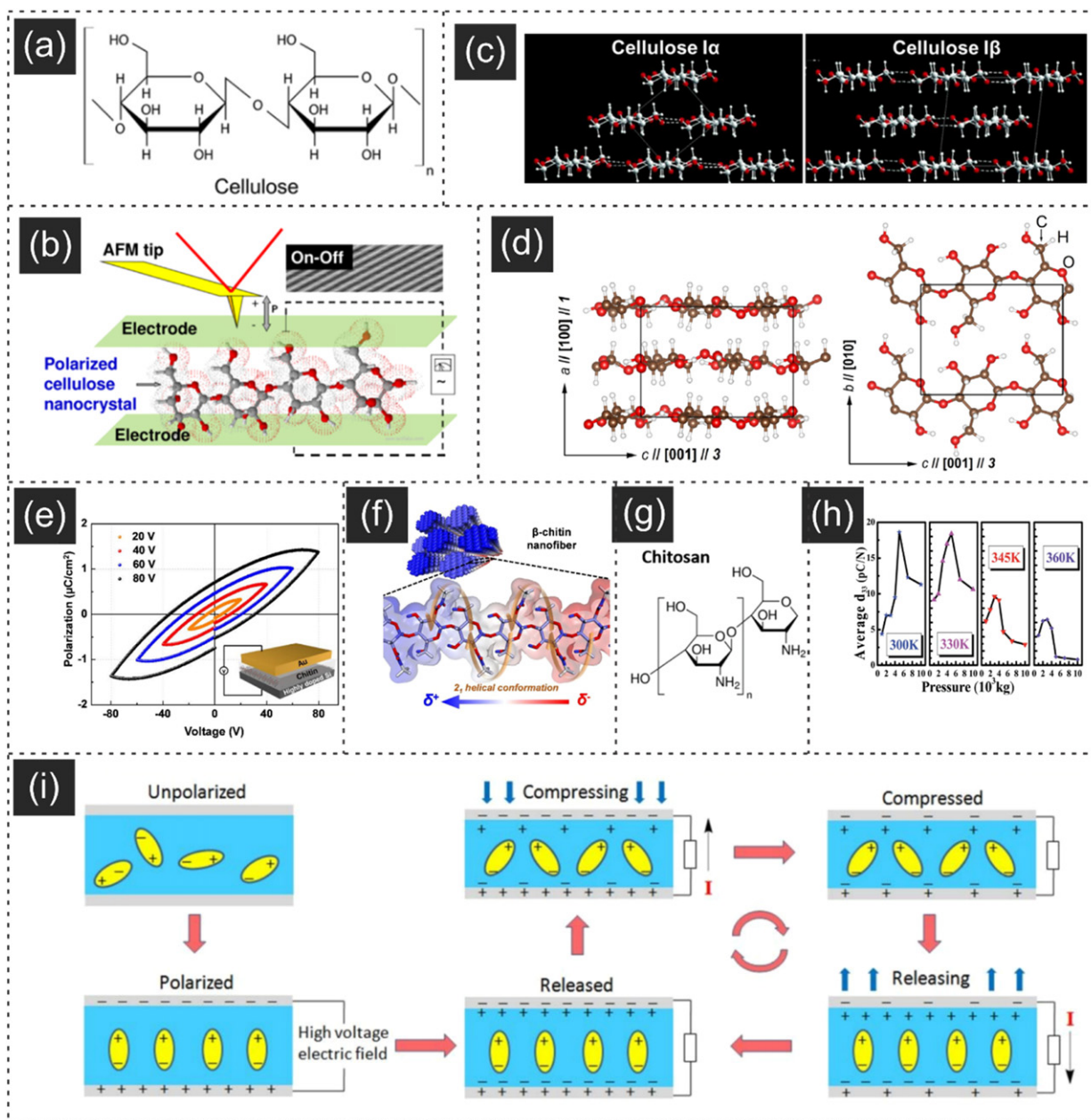


Fig. 14 (a) 3D and 2D structure formula of cellulose, (b) Schematic of piezoelectric phenomena of cellulose nanocrystal thin films and the piezoelectric force microscope image, (c) two polymorphs (I_α and I_β) existing in cellulose I, (d) projected structure of cellulose I_β (space group $P2_1$) along the b and a axis, showing a layered structure of I_β clearly along the a axis, and weaker bonding along the b axis with respect to bonding along the c axis, (e) P-E hysteresis loops of chitin thin film, and (inset) schematic of the ferroelectric device structure, (f) spontaneous polarization of β -chitin nanofibers, (g) chitosan molecular structure, (h) d_{33} coefficient formation of chitosan from various pressures and sintering temperatures, and (i) working mechanism diagram of a typical PENG device. Reproduced from Rajinipriya, M., Nagalakshmaiah, M., Robert, M., Elkoun, S., 2018. Importance of agricultural and industrial waste in the field of nanocellulose and recent industrial developments of wood based nanocellulose: A review. *ACS Sustain. Chem. Eng.* 6, 2807–2828. Csoka, L., Hoeger, I.C., Rojas, O.J., *et al.*, 2012. Piezoelectric effect of cellulose nanocrystals thin films. *ACS Macro Lett.* 1, 867–870. Beaumont, M., 2017. PhD Thesis: Characterization and Modification of a Cellulose II Gel. Dri, F.L., Shang, S., Hector, L.G., *et al.*, 2014. Anisotropy and temperature dependence of structural, thermodynamic, and elastic properties of crystalline cellulose I_β : A first-principles investigation. *Model. Simul. Mater. Sci. Eng.* 22, 085012. Kim, K., Ha, M., Choi, B., *et al.*, 2018b. Biodegradable, electro-active chitin nanofiber films for flexible piezoelectric transducers. *Nano Energy* 48, 275–283. Praveen, E., Murugan, S., Jayakumar, K., 2017. Investigations on the existence of piezoelectric property of a bio-polymer – chitosan and its application in vibration sensors. *RSC Adv.* 7, 35490–35495. Song, Y., Shi, Z., Hu, G.-H., *et al.*, 2021. Recent advances in cellulose-based piezoelectric and triboelectric nanogenerators for energy harvesting: A review. *J. Mater. Chem. A* 9, 1910–1937.

Chitin and chitosan

Chitin is an important polysaccharide with N-acetylglucosamine units that are produced by nematodes, arthropods and fungi. It functions normally as scaffold material for supporting cuticles of the epidermis and trachea (Muskovich and Bettinger, 2012). Chitosan is also a polysaccharide similar to sugar that makes up 1–4 linked 2-acetamido-2-deoxy- β -D-glucopyranose and 2-amino-2-deoxy- β -D-glucopyranose. It can be obtained from the hard-outer skeleton of shrimp, lobster and crab, and also the deacetylation of chitin. Chitosan has excellent biocompatibility and biodegradability and antifungal effect. Accordingly, it is attractive for use in biomedical applications, especially wound dressing, wound healing and tissue engineering. Both chitin and chitosan have been characterized as organic piezoelectric material, and the β -crystalline structure of chitin also shows spontaneous polarization with P–E hysteresis loops, as shown in Fig. 14(e) and (f) (Kim *et al.*, 2018b). According to its molecular structure (Fig. 14(g)), chitosan contains many polar covalent bonds that can generate dipoles. Therefore, the piezoelectric response of chitosan is dictated generally by an internal structure of polar crystalline phases, with dipole orientation involving hydroxyl ($-\text{OH}$), amine ($-\text{NH}-$) and amide ($-\text{CONH}-$) functional groups (Hu *et al.*, 2021). Chitosan exhibits a piezoelectric constant of $19.03 \pm 6.80 \text{ pC} \cdot \text{N}^{-1}$ at 300K (Fig. 14(h)) without external electric field induction (Praveen *et al.*, 2017). It also has been reported that by adding chitosan as filler (15 wt%) into collagen, the piezoelectric strain, d_{14} , of collagen could be increased from $0.096 \text{ pC} \cdot \text{N}^{-1}$ to $0.212 \text{ pC} \cdot \text{N}^{-1}$ (Silva *et al.*, 2001). However, it has not been reported until now whether piezoelectricity of both chitin and chitosan can be enhanced by control of processing. Importantly, all crucial piezoelectricity of the polysaccharide-based materials (increased directional dipoles and controlled polarization) are effective for efficient energy harvesting, which can be made as a piezoelectric nanogenerator, according to the mechanism in Fig. 14(i).

Protein-based materials

Special protein-based materials such as collagen, silk fibers and some peptides exhibit intrinsic piezoelectric behavior, where perpendicular electric polarization occurs from external mechanical stress. This is attributed to the uneven distribution of carbon atoms and varied polarization charged atomic groups, associated with anisotropic asymmetric crystal structure.

Collagen

Collagen is the most abundant protein in mammals, accounting for 25%–35% of all proteins in the body. The main triple-helix structure is found in the extracellular matrix of various tissues such as bones, cartilage, ligaments, tendons and skin. A single collagen molecule is composed of more than 1000 amino acids bound together to form a collagen helix, which comprises three elongated α -helix fibril chains. A short piece of collagen molecule, displaying a 7-residue-long amino acid sequence (Pro-Gly-Asn-Asp-Gly-Ala-Lys) in chain C is shown in Fig. 15(a). Collagen is a well-known organic material that mainly causes piezoelectric effect in the bone. However, its fundamental principle has still not been discovered clearly. It has been proposed that the origin of piezoelectricity in collagen involves non-centrosymmetry in the $\text{C}=\text{O}-\text{NH}$ bond at the molecular level (Zhou *et al.*, 2016b). The polar-bond $\text{C}=\text{O}-\text{NH}$ reorients in the α -helix structure, resulting in permanent dipoles with high-order polarization in collagen (Bystrov *et al.*, 2012). Then, the individually charged permanent dipole reorients under mechanical stress towards the long axis of the collagen chain, resulting in its piezoelectricity. This is illustrated in Fig. 15(b), displaying the vector changes in the dipole-moment before and after uniaxial tension (Zhou *et al.*, 2016b). The red and blue arrows indicate the direction and magnitude of the dipole moment vectors, respectively. The shear piezoelectric constant of d_{14} for impregnated collagen by tendon and bone varies from 0.2 to $2.0 \text{ pC} \cdot \text{N}^{-1}$ (Fukada, 2000), and even more when adding chitosan, or by adjusting the pH from acidic to neutral.

M13 bacteriophage

The M13 bacteriophage has emerged recently as an organic piezoelectric material for energy harvesting applications and sensors. It has a well-defined structure of 6.6 nm in diameter and 880 nm in length, wrapped up in ~ 2700 copies of major coated protein (pVIII), with 5 copies (pIII/pVI) on the top and (pVIII/pIX) on the bottom of minor proteins (Moon *et al.*, 2017). The schematic structure of the M13 bacteriophage, with vertically aligned nanopillars, is illustrated in Fig. 15(c). The major protein is anchored to a single-stranded DNA with $\sim 20^\circ$ tilt angle respective to the DNA axis. Net polarization from the pIX to pIII protein is not zero because each pVIII has a permanent dipole moment directly from the tail (Shin *et al.*, 2015). The rainbow arrow in Fig. 15(c) indicates the dipole direction. Accordingly, the piezoelectricity of M13 bacteriophage is due to phage nanopillar deformation in both the axial and radial direction (Shin *et al.*, 2015). The values of d_{33} for the axial and radial direction are $\sim 23.4 \text{ pm} \cdot \text{V}^{-1}$ and $\sim 7.8 \text{ pm} \cdot \text{V}^{-1}$ (Lee *et al.*, 2012), respectively. The d_{33} for axial direction improves by three times from the radial direction (Shin *et al.*, 2015). Moreover, the dipole strength of the M13 bacteriophage can be modified by modulating the glutamate number between the 1st and 5th amino acids at the tail, as illustrated in Fig. 15(d). Lee *et al.* (2019b) recently improved the d_{33} for axial direction by up to $\sim 26.4 \text{ pm} \cdot \text{V}^{-1}$.

Silk

Silk is an organic protein polymer generated by more than four hundred species of insects. It is a semicrystalline polymer with unique properties such as remarkable strength and versatility. Silk has been exploited in many forms, *i.e.*, nanofibers, nanoparticles, microspheres, hydrogels and films, for utilization as biomaterials for various biomedical applications. The molecular structure of silk is composed of repeating units of amino acid, with the presence of N, O and S atoms in its backbone. Silk has a combination of amorphous and crystalline phases. In its crystalline part, β -platelet sheets and a helical- α elastic structure of amino

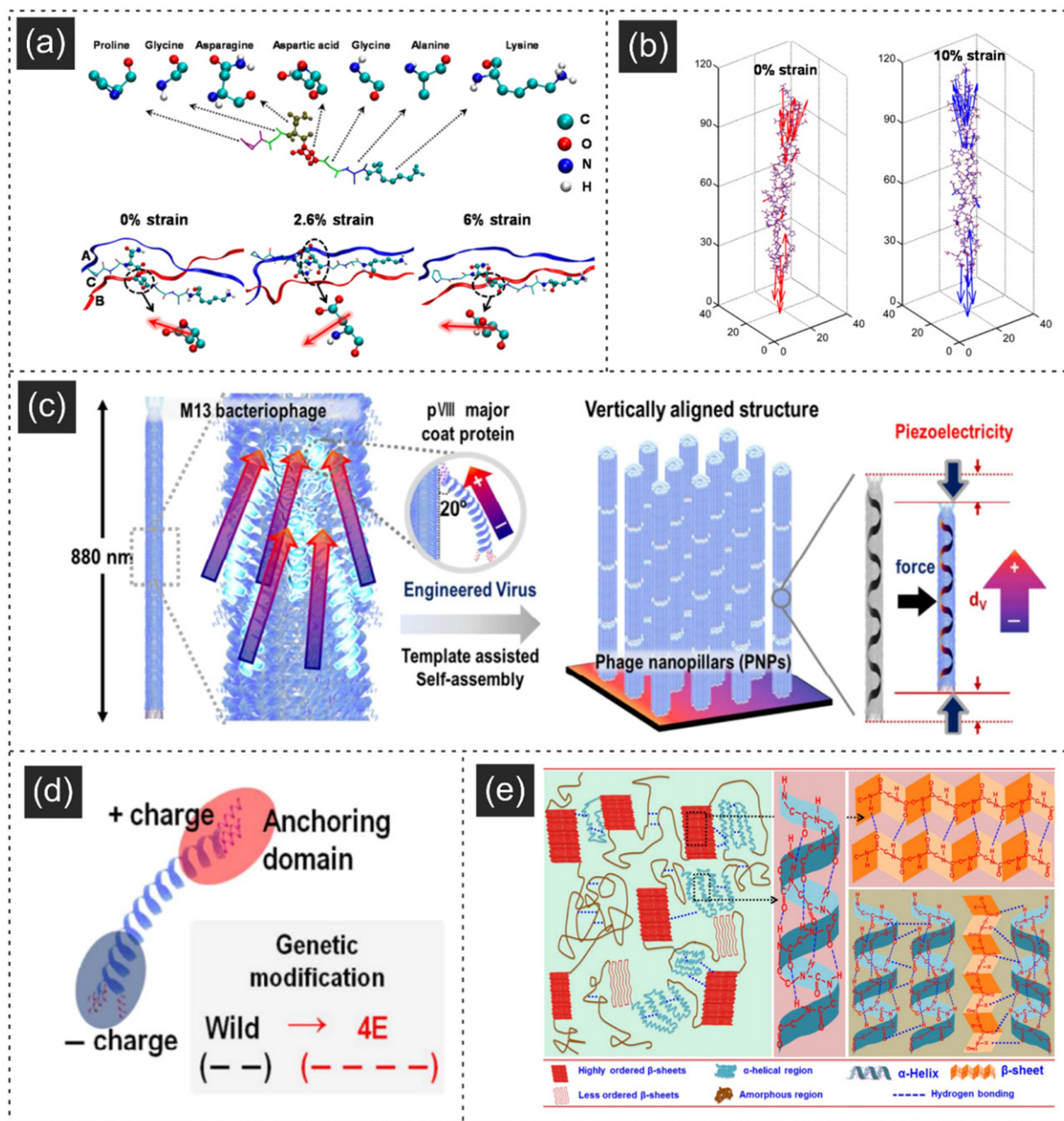


Fig. 15 (a) Short piece of collagen molecule, displaying a 7- residue-long amino acid sequence (Pro-Gly-Asn-Asp-Gly-Ala-Lys) in chain C, (b) molecular origin of the piezoelectric effect in collagen, (c) schematic illustration of M13 bacteriophage, (d) schematic representation of a single pVIII major coated protein. The dipole strength can be modified by modulating the number of glutamates between the first and fifth amino acids in the tail region, (e) higher crystalline zone β -sheet, lower crystalline zone β -sheet, amorphous zone and α -helical region present in SS, drawn schematically. The chemical structure of α -helix (pink) and β -sheet (purple) presenting in SS (brown) and possible intra- and inter-molecular interaction of α -helices and β -sheets through H-bonding. Reproduced from Zhou, Z., Qian, D., Minary-Jolandan, M., 2016b. Molecular mechanism of polarization and piezoelectric effect in super-twisted collagen. *ACS Biomater. Sci. Eng.* 2, 929–936. Shin, D.-M., Han, H.J., Kim, W.-G., *et al.*, 2015. Bioinspired piezoelectric nanogenerators based on vertically aligned phage nanopillars. *Energy Environ. Sci.* 8, 3198–3203. Karan, S.K., Maiti, S., Kwon, O., *et al.*, 2018. Nature driven spider silk as high energy conversion efficient bio-piezoelectric nanogenerator. *Nano Energy* 49, 655–666.

acids are interconnected strongly with each other through intra- and inter-molecular H-bonding (Karan *et al.*, 2018), according to the schematic diagram in Fig. 15(e). The asymmetric carbon atom in amino acid groups, and highly ordered alignment, result in electrical dipole generation inside the lattice.

Therefore, silk can exhibit piezoelectric response due to β -sheet crystallinity and crystalline orientation (Yucel *et al.*, 2011). Silk films with a silk II (β -sheet crystalline phase) ratio of 2.4 exhibit shear piezoelectric coefficients of d_{14} of $-1.5 \text{ pC} \cdot \text{N}^{-1}$ and d_{33} of

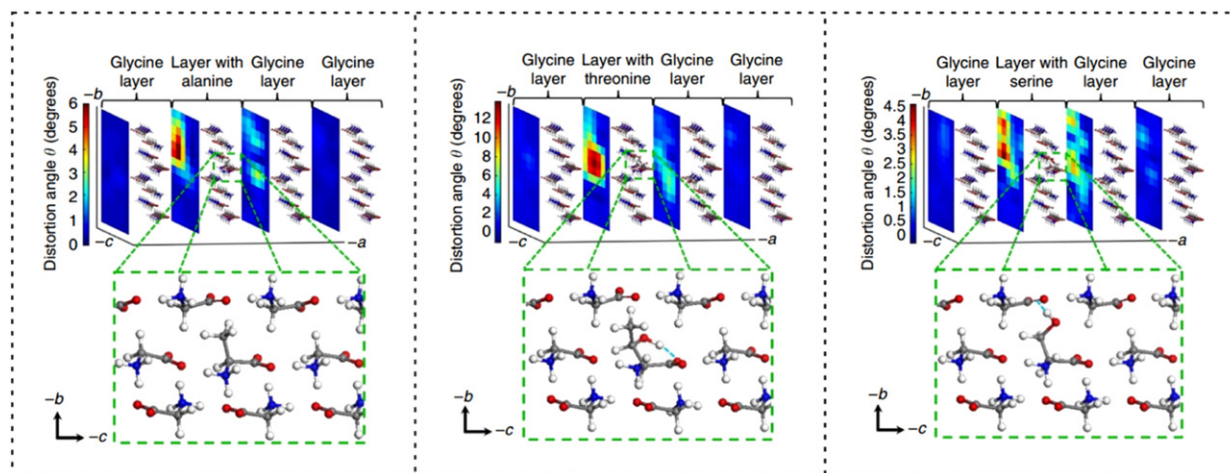


Fig. 16 Most stable DFT conformation computed for each system, together with a three-dimensional intensity map depicting molecular distortion in the unit cell, with colors representing the dopant-induced distortion angle of the nitrogen to carboxylic carbon vector, relative to its orientation in the undoped glycine crystal (note the different scale for each system). Reproduced from Meirzadeh, E., Azuri, I., Qi, Y., *et al.*, 2016. Origin and structure of polar domains in doped molecular crystals. *Nat. Commun.* 7, 13351.

$56.7 \text{ pm} \cdot \text{V}^{-1}$ (Joseph *et al.*, 2016). The piezoelectric response was also recorded *via* the tip bias (-10 to 10 V) from AFM, demonstrating the hysteresis loop with a sharp (180°) turn at the coercive voltage of -1.5 V and 0.9 V (Joseph *et al.*, 2016). This sensitivity corresponds to the calculated d_{33} of $126.3 \text{ nm} \cdot \text{V}^{-1}$ (Joseph *et al.*, 2016). The piezoelectric silk can potentially enable development of bio-microelectromechanical systems (MEMS) as well as bio-portable/wearable sensors and harvesters.

Peptides and amino acids

A huge number of amino acids and peptides have been crystallized (Vijayakanth *et al.*, 2019), presenting new opportunities for energy harvesting and sensors. Diphenylalanine (FF) peptide is consisted of two phenylalanine (F) amino acids. It can be self-assembled into the semi-crystalline phase, thus exhibiting high biocompatibility, functional and morphological diversity with high Young's modulus (Jenkins *et al.*, 2018). The nanostructured diphenylalanines, *i.e.*, nanorods, nanotubes and nanosphere, with a non-centrosymmetric hexagonal space group are studied widely (Jenkins *et al.*, 2018). By using the self-assembly process driven by meniscus, the unidirectionally polarized FF peptide nanotubes are aligned. A high shear piezoelectric constant (d_{15}) of $\sim 60 \text{ pm} \cdot \text{V}^{-1}$ is achieved (Chorsi *et al.*, 2019). In addition, the piezoelectric constant, d_{33} , reaches up to $\sim 17.9 \text{ pm} \cdot \text{V}^{-1}$ for vertical alignment with the microrod peptide. Lysozyme, a well-known globular protein, was reported as piezoelectric material exhibiting piezoelectricity in crystalline forms. Nucleobase morpholino β -amino acids with adenine and thymine also showed piezoelectricity and ferroelectricity within their crystalline forms. Generally, amino acid crystals primarily stabilize in non-centrosymmetric monoclinic and orthorhombic space groups, leading them to exhibit piezoelectricity.

Glycine is the most important piezoelectric amino acid nowadays. It is a zwitterionic amino acid which crystallizes in three distinct symmetries of alpha (α), beta (β) and gamma (γ) phases (Guerin *et al.*, 2018). The two phases of β - and γ -glycine display piezoelectricity, due to their acentric structures, arising from atom displacement in the crystal lattice. Such a displacement at the molecular level creates a dipole in local structure, resulting in non-zero net polarization in bulk. The molecular dipoles contributing to β - and γ -glycine, and spontaneous polarization along the 3-axis, relates to the longitudinal 33 piezoelectric coefficients (Guerin *et al.*, 2018). Meanwhile, α -glycine is the only a glycine structure that precludes piezoelectric properties due to its centrosymmetric structure. β -glycine has the highest response to the shear piezoelectric constant (d_{16}) of $\sim 190 \text{ pm} \cdot \text{V}^{-1}$ and $d_{33} = 178 \text{ pC} \cdot \text{N}^{-1}$ (Guerin *et al.*, 2018), which is comparable to that of the famous piezoelectric oxide BaTiO_3 . However, the β -phase is unstable in ambient conditions and can change spontaneously into the α - or γ -phase. In addition, it was reported that fabricating a glycine piezoelectric device by placing small γ -glycine crystals between two copper film electrodes can generate a maximum open-circuit voltage (V_{OC}) of 0.45 V upon a forcing load of 0.17 N . Furthermore, mixing glycine in the presence of L- α -amino acids (for example, threonine, serine or alanine) can reduce the centrosymmetric structure of the host glycine amino acid and create highly polar domains (Meirzadeh *et al.*, 2016). Residual dopants, even a tiny amount of around $0.5 \text{ wt\%}$, in the L and L' sites can induce polarization in the b direction, thus producing a high dipole moment of about 14.9 . Glycine with alanine also shows polarization of $8.6 \times 10^{-9} \text{ C} \cdot \text{cm}^{-2}$ along the b axis, and glycine with serine provides $1.2 \times 10^{-9} \text{ C} \cdot \text{cm}^{-2}$, according to the density functional theory (DFT) calculation (Meirzadeh *et al.*, 2016). Fig. 16 shows the calculated, most stable structure according to DFT, together with a three-dimensional intensity map depicting molecular distortion relative to pure glycine crystal. In 2021, silk protein was used as a filler in the chitosan biopolymer matrix. This composite showed the highest electrical output for both V_{OC} and I_{SC} (Charoonsuk *et al.*, 2021). As silk contains more glycine than two other proteins studied (egg shell membrane and albumin), it provides more charges (Charoonsuk *et al.*, 2021). In addition, several aromatic L-amino acids such as 3,4-dihydroxyphenylalanine (L-DOPA), L-tyrosine (L-Tyr) and L-phenylalanine (L-Phe) are known to form a non-centrosymmetric

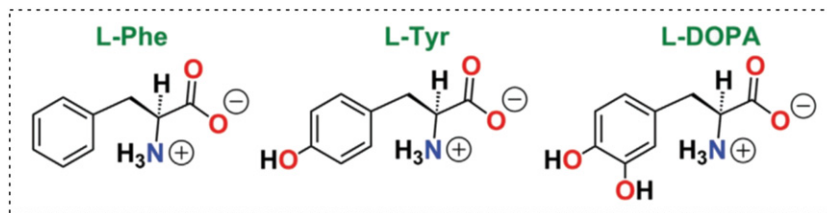


Fig. 17 Molecular structure of L-Phe, L-Tyr and L-DOPA. Reproduced from Vijayakanth, T., Liptrot, D.J., Gazit, E., *et al.*, 2022. Recent advances in organic and organic–inorganic hybrid materials for piezoelectric mechanical energy harvesting. *Adv. Funct. Mater.* 32, 2109492.

structure from packed hydrogen-bonded assemblies. The molecular structure of L-Phe, L-Tyr and L-DOPA are illustrated in **Fig. 17** (Vijayakanth *et al.*, 2022). Seven other smallest (non-glycine) monoclinic L-amino acid crystals, including the crystal packing, monoclinic angle, and highest predicted piezoelectric strain constant, are reported (Guerin *et al.*, 2018). These molecular recognitions are formed *via* distinct hydrogen bond dimer, with high thermal stability ($\approx 581\text{K}$) and unusual water solubility.

Structural Designs for the PENG

Various structural designs of the PENG are required for suitability in diverse applications situations. The initial design of PENG was the in-plane structure, comprising of the piezoelectric layer sandwiched between metal electrodes (**Fig. 4(a)**). This has attracted interest from many researchers (Shin *et al.*, 2014; Liu *et al.*, 2016a; Choi *et al.*, 2017; Sriphan *et al.*, 2018; Charoonsuk *et al.*, 2019) due to advantages such as facile fabrication, low-cost, and easy modification of the active piezoelectric layer.

In one of the most widely studied/traditional piezoelectric materials, ZnO NWs were grown on a rigid substrate prior to the subsequent encapsulation with the protecting polymeric films, leading to PENG device to harvest/sense energy (Shin *et al.*, 2014; Liu *et al.*, 2016a; Choi *et al.*, 2017). Choi *et al.* (2017) prepared the hybrid piezoelectric ZnO NWs/PVDF film as depicted in **Fig. 18(a)**. This hybrid structure delivered maximum electrical outputs of approximately 0.4 V and 28 nA at 3.2% of applied strain. The idea of incorporating various micro/nanomaterials into a polymer matrix to form piezoelectric composite film has spread widely, thanks to significant enhancements of PENG performance. Huan *et al.* (2018) fabricated the high-performance PENG by using the (K, Na)NbO₃ (KNN) particles/Ag NPs/multi-walled carbon nanotubes (MW-CNTs) heterostructure (**Fig. 18(b)**). Utilizing multi-phase coupling and poling aid, this PENG generated outstanding voltage and current signals of $\sim 240\text{ V}$ and $\sim 23\text{ }\mu\text{A}$, respectively. With an instantaneous output power of 1.1 mW, it showed higher performance than the previously reported lead-free composite-based PENG. In addition, a piezoelectric device could be fabricated using interdigital electrodes (IDEs) to directly collect piezoelectric charges from piezoelectric materials. As reported by Sriphan *et al.* (2018) in **Fig. 18(c)**, BT fibers prepared from the electrospinning process were dispersed onto the IDEs, followed by BT powders. The fabricated sample was finally encapsulated with PDMS. It was found that incorporation of BT powders could boost the output performance of the device 3-fold in both voltage and current outputs, compared with the BT powder-free sample. In another development, cantilever beam is an attractive element in PENG for harvesting low-vibrational energy. Several studies have utilized the cantilever substrate coated with traditional ceramic materials based on PZT (Dechant *et al.*, 2017; Du *et al.*, 2020; Kim *et al.*, 2016; Song *et al.*, 2015). The unique and interesting work was demonstrated by Nan *et al.* (2021), who directly used lead-free 2D NSs as a piezoelectric cantilever layer (**Fig. 18(d)**). Other 2D nanomaterials such as boron nitride (BN) and MX₂ ($M = \text{Mo or W}$, and $X = \text{S, Se or Te}$) were also deposited on silicon substrate to form a cantilever beam structure. The highest piezoelectric constant was reported from MoTe₂ NSs, delivering the maximum output power of 1.42 nW. The proposed device showed a higher performance than the graphene-like ZnO nanogenerator, demonstrating high potential for practical usages. Besides the cantilever structure for harvesting low-frequency excitation, spring-based PENG has also been developed. Su *et al.* (2021) designed a 3D piezoelectric spring consisting of a layered Al electrode, electrospun PVDF fiber, and a Pt electrode, as shown in **Fig. 18(e)**. A single PENG unit can deliver up to 2 V and 80 nA electrical outputs, which could be increased to 7.2 V and 300 nA for three units. Importantly, this prototype is capable of multifunctional sensing including strain, frequency, speed and resistance. **Fig. 18(f)** shows a simple piezoelectric spring device forming a pendulum oscillator. In this system, common binder clips coated with piezoelectric materials were connected together. The proposed PENG in the pendulum structure could efficiently detect an ultra-low frequency, as well as multi-directional vibration energy with the highest output power of $\sim 13\text{ mW}$ at low frequency operation, thus providing a great opportunity for a low-cost power supply and sensing unit.

PENG technology can also scavenge surrounding wave energies such as water, wind and sound. These flow energies are of practical importance in remote and hilly areas. The incoming waves cause fluctuation and bending of the piezoelectric layer in the PENG structure. Accordingly, the device performance depends on energy level, frequency and operational period (Kim *et al.*, 2011). Zhang *et al.* (2017) proposed a rotational wind energy harvester based on the piezoelectric effect. The PVDF cantilever beams were embedded inside a plastic tube, where turntable blades caused an impact-induced vibration energy (**Fig. 19(a)**). More than 200 V could be achieved when the wind speed was above $10\text{ m}\cdot\text{s}^{-1}$, indicating that the output performance depends on critical factors such as impact frequency and wind speed. Furthermore, even a small level of wind flow can be harvested using a

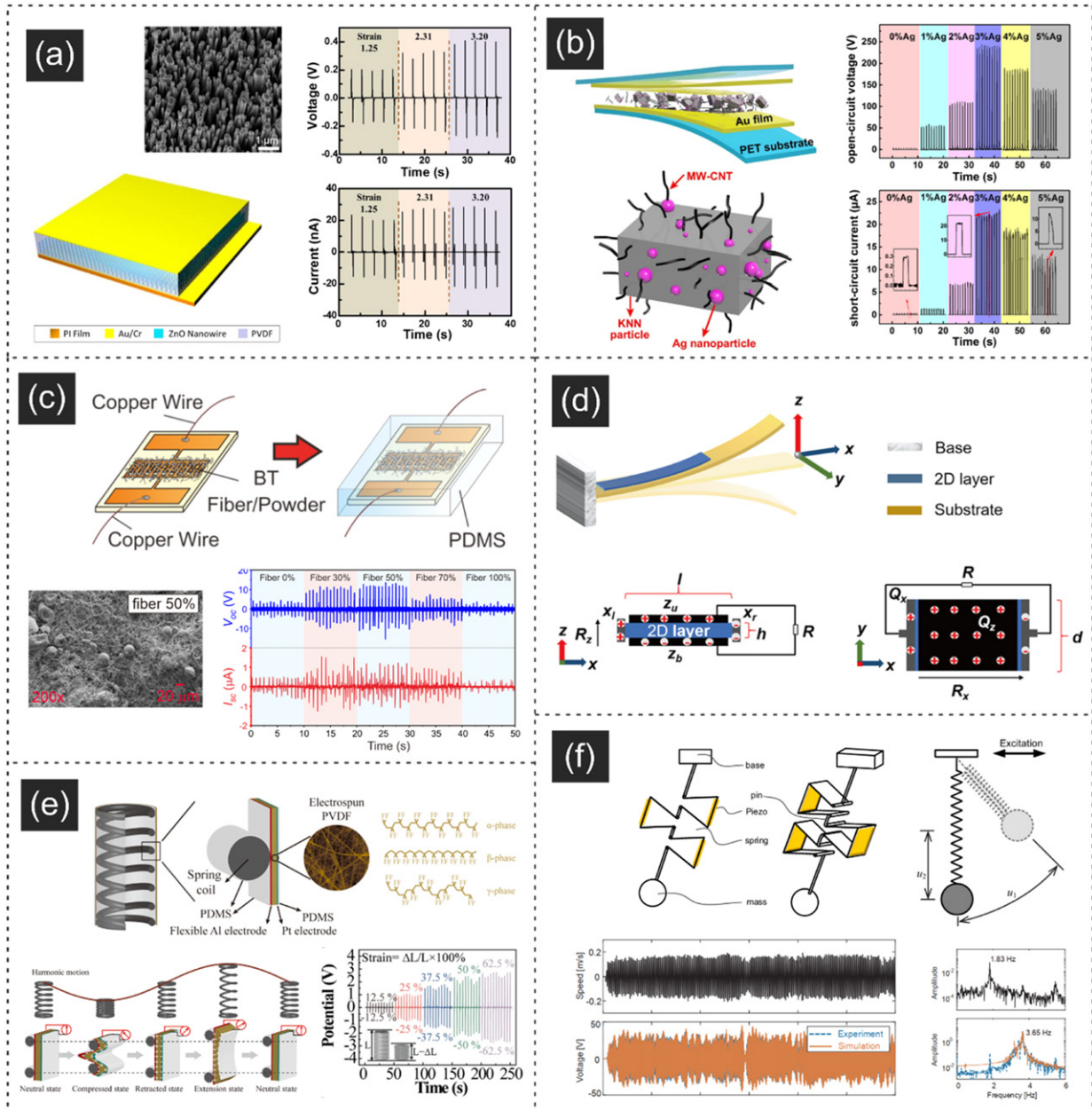


Fig. 18 Structural designs of an in-plane structure PENG (a) PVDF/ZnO NWs, (b) KNN particles/Ag NPs/MW-CNTs and (c) BT fibers/BT powder hybrid systems. Other structures include (d) a cantilever structure based on 2D dielectric materials, (e) a 3D piezoelectric spring with electrospun PVDF layer, and (f) spring pendulum oscillator with piezoelectric ceramic layer. Reproduced from Choi, M., Murillo, G., Hwang, S., *et al.*, 2017. Mechanical and electrical characterization of PVDF-ZnO hybrid structure for application to nanogenerator. *Nano Energy* 33, 462–468. Huan, Y., Zhang, X., Song, J., *et al.*, 2018. High-performance piezoelectric composite nanogenerator based on Ag/(K,Na)NbO₃ heterostructure. *Nano Energy* 50, 62–69. Sriphan, S., Nawani, C., Vittayakorn, N., 2018. Influence of dispersed phase morphology on electrical and fatigue properties of BaTiO₃/PDMS nanogenerator. *Ceram. Int.* 44, S38–S42. Nan, Y., Tan, D., Shao, J., *et al.*, 2021. 2D materials as effective cantilever piezoelectric nano energy harvesters. *ACS Energy Lett.* 6, 2313–2319. Su, Y., Li, Q., Amagat, J., Chen, M., 2021. 3D spring-based piezoelectric energy generator. *Nano Energy* 90, 106578. Wu, Y., Qiu, J., Zhou, S., *et al.*, 2018. A piezoelectric spring pendulum oscillator used for multi-directional and ultra-low frequency vibration energy harvesting. *Appl. Energy* 231, 600–614.

flutter-structured PENG as presented by Pandey *et al.* (2019). Using La-doped ZnO NRs/PDMS composite with a small size of 2.3 cm² (Fig. 19(b)), this flutter PENG produced an output voltage of ~1.6 V which is three times higher than the original PENG. This result indicated great potential for not only an energy harvester but also a wind velocity sensor.

The development of implantable medical devices, especially a cardiac pacemaker, is challenging as one needs to consider several critical characteristics such as biocompatibility, toxicity, and ability to self-power (Li and Wang 2017). A conventional

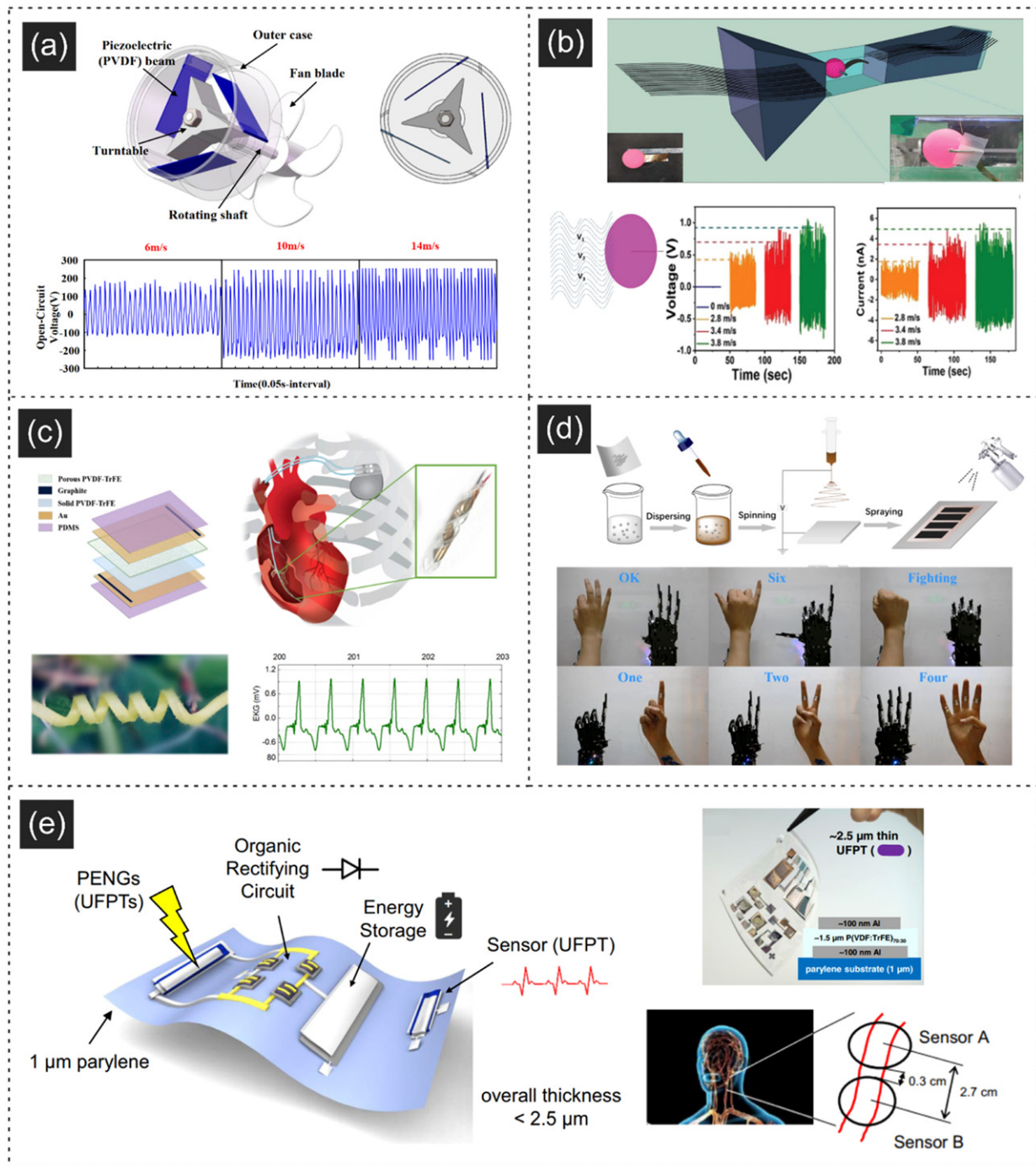


Fig. 19 Structural designs of PENG using (a) a rotational structure with PVDF beams, (b) flutter structure based on the ZnO NRs/PDMS composite, (c) helical structure with flexible porous PVDF-TrFE film, (d) an ultra-flexible ZnO NFs/PVDF film, and (e) ultra-flexible ferroelectric transducer and electronic systems. Reproduced from Zhang, J., Fang, Z., Shu, C., *et al.*, 2017. A rotational piezoelectric energy harvester for efficient wind energy harvesting. *Sens. Actuator A: Phys.* 262, 123–129. Pandey, R., Khandelwal, G., Palani, I.A., *et al.*, 2019. A La-doped ZnO ultra-flexible flutter-piezoelectric nanogenerator for energy harvesting and sensing applications: A novel renewable source of energy. *Nanoscale* 11, 14032–14041. Dong, L., Closson, A.B., Oglesby, M., *et al.*, 2019. In vivo cardiac power generation enabled by an integrated helical piezoelectric pacemaker lead. *Nano Energy* 66, 104085. Deng, W., Yang, T., Jin, L., *et al.*, 2019. Cowpea-structured PVDF/ZnO nanofibers based flexible self-powered piezoelectric bending motion sensor towards remote control of gestures. *Nano Energy* 55, 516–525. Petritz, A., Karner-Petritz, E., Uemura, T., *et al.*, 2021. Imperceptible energy harvesting device and biomedical sensor based on ultraflexible ferroelectric transducers and organic diodes. *Nat. Commun.* 12, 2399.

pacemaker is formed typically in a plate-like structure (Azimi *et al.*, 2021; Li *et al.*, 2019; Li and Wang, 2017). However, a novel design provides prominent points in high compatibility with human organs and does not require placement surgery. Dong *et al.* (2019) designed flexible porous PVDF-TrFE piezoelectric thin films in an integrated helical configuration, coupled with current lead, as depicted in Fig. 19(c). The helical piezoelectric sensor could simulate right ventricular motions and other extensive tests for heart rate cycling. A matrix of the piezoelectric elements could charge the pacemaker battery well. The proposed idea provides a sustainable power source for pacemakers or any other implantable devices. In order to design IoT systems and robotic controls, piezoelectric materials are required to be in thin-film form, ultra-flexible, of low-cost, easily fabricated, and to possess high sensitivity (Liu *et al.*, 2021). Deng *et al.* (2019) prepared a self-powered PENG based on cowpea-structured PVDF/ZnO NFs composites, as shown in Fig. 19(d). The fabricated piezoelectric sensor could remote control gestures in human-machine interfaces, exhibiting excellent sensitivities up to $0.33 \text{ V} \cdot \text{kPa}^{-1}$ and $4.4 \text{ mV} \cdot \text{deg}^{-1}$ in pressing and bending motions, respectively. To construct a complete system, PENG is a power/sensing unit that needs to be assembled with other electronic nodes such as AC/DC converter, signal filter, and storage unit. Nevertheless, combining all essential electronic nodes into a single unit is a challenging task. Petritz *et al.* (2021) proposed all-in-one 3D electronic objects mounted onto an ultrathin substrate as a ferroelectric polymer transducers in e-health patch form (Fig. 19(e)). The Ultra-thin PVDF-TrFE polymer (on top of flexible perylene substrate) could produce maximum power density of $3 \text{ mW} \cdot \text{cm}^{-3}$. The synergetic effect among electronic nodes efficiently monitors pulse and blood pressure without the need to connect external electronic components. The proposed concept opens the route for sufficient use of wireless electronic systems, especially those that interact with the human body.

Recent Progress of PENG Applications

Energy Harvesting and Sensing From the Natural Environment

Energies surrounding us are in various forms including mechanical compressing/elongation, sound, vibration, wind, water flow, *etc.* They have the potential of being alternative energy sources for harvesting and sensing in various technologies (Cao *et al.*, 2021; Akin-Ponnle and Carvalho, 2021; Covaci and Gontean, 2020). Accordingly, PENG can serve several applications depending on the operating mechanism and device design. Selected examples of energy harvesting and sensing by the PENG in ambient environment are followed.

Ye *et al.* (2019) prepared the piezoelectric nanocomposite of PVDF-TrFE/BNNTs micropillar arrays, as shown in Fig. 20(a). With 0.3 wt% of BNNTs, the maximum output voltage reached up to 22 V, and the maximum output current of $\sim 0.6 \mu\text{A}$ could be achieved. The outputs obtained were 11-fold higher than the pristine PVDF-TrFE film and showed excellent sensitivity of $\sim 55 \text{ V} \cdot \text{MPa}^{-1}$. In practice, the devices could be a reliable power generator from simple human movements, producing a large output voltage of $\sim 100 \text{ V}$ in foot stepping conditions. Also, high radiation shielding of prepared composite provides promising spaced-out candidate utilization. Unwanted noise occurs especially in industrial factories and on highways with heavy traffic. Hence, scavenging or sensing noise is of interest for waste energy management. Cha *et al.* (2010) demonstrated the possibility of fabricating a sound-driven power generator by using aligned ZnO NW arrays (Fig. 20(b)). By applying approximately 100 dB of sound wave to the PENG, clear AC output voltage of $\sim 50 \text{ mV}$ could be detected. In fact, vibrational energy in general can be similarly harvested by using the piezoelectric effect. Deng *et al.* (2018) presented a newly designed elastic fork-shaped piezoelectric cantilever with ZnO NRs as shown in Fig. 20(c). The peak values of about 160 mV and 11 nA for output voltage and current, respectively, were recorded. The dual-beam piezoelectric cantilever showed high sensitivity for vibration energy harvesting at low frequency ($\sim 13 \text{ Hz}$ corresponding to resonance frequency), simple fabrication, and capability of controlling the shape of substrate. PENG could also be fabricated in the form of a turbine to scavenge not only wind energy but also water waves. Egbe *et al.* (2021) proposed a magnetic-assisted vibrational turbine PENG, harvesting energy in amphibious conditions (Fig. 20(d)). The structure comprised of 3D-printed turbines, blades and anchor systems. Magnetic parts attached to a frame played the role of inducing vibration/impact of PVDF rubber strips inside a rotating core. The turbine PENG generated output power of $9 \mu\text{W}$ for each piezoelectric strip at 4 Hz of rotating frequency. Also, the device could adapt well to air and water, harvesting the field energy flow of both environments. Rapid developments in industry and the community, including chemicals in industrial productions, have led to concern of air and water pollution that directly affects the health of human (Dhall *et al.*, 2021). An example of this is hydrogen sulfide (H_2S), which is flammable, toxic, corrosive, and hazardous to humans (Urasinska-Wojcik *et al.*, 2016; Qu *et al.*, 2016). Hence, gas sensing techniques in different configurations are highly essential. Utilizing PENG for H_2S sensing is possible by using metal oxide nanowires as an active layer. Qu *et al.* (2016) prepared a heterojunction NiO/ZnO NWs PENG as a self-powered gas sensor (Fig. 20(e)). It was found that the output voltage decreased linearly from 0.39 V (dry air) to 0.06 V (1000 ppm of H_2S). A high sensing performance is due to the coupling between piezoelectric effect of ZnO NWs and p-n junction in the form of a heterojunction. Catechol detection is another example of environmental monitoring. Catechol is a phenolic compound widely used in medical chemicals, food agents, cosmetics and dyes, which might be left as a residue in the environment (Yin *et al.*, 2011). This hazardous compound can be absorbed into the gastrointestinal tract and accumulated to bone marrow, causing organ failure, cancer, *etc.*, (Irons, 1985). Catechol detection can be similarly achieved using PENG as a self-powered sensor. Abisegapriyan *et al.* (2020) presented a tube-like chemical-sensing device using BiFeO_3 NPs which combines piezoelectric generation and catechol detection (Fig. 20(f)). A flow of catechol solution delivered a variable electrical signal

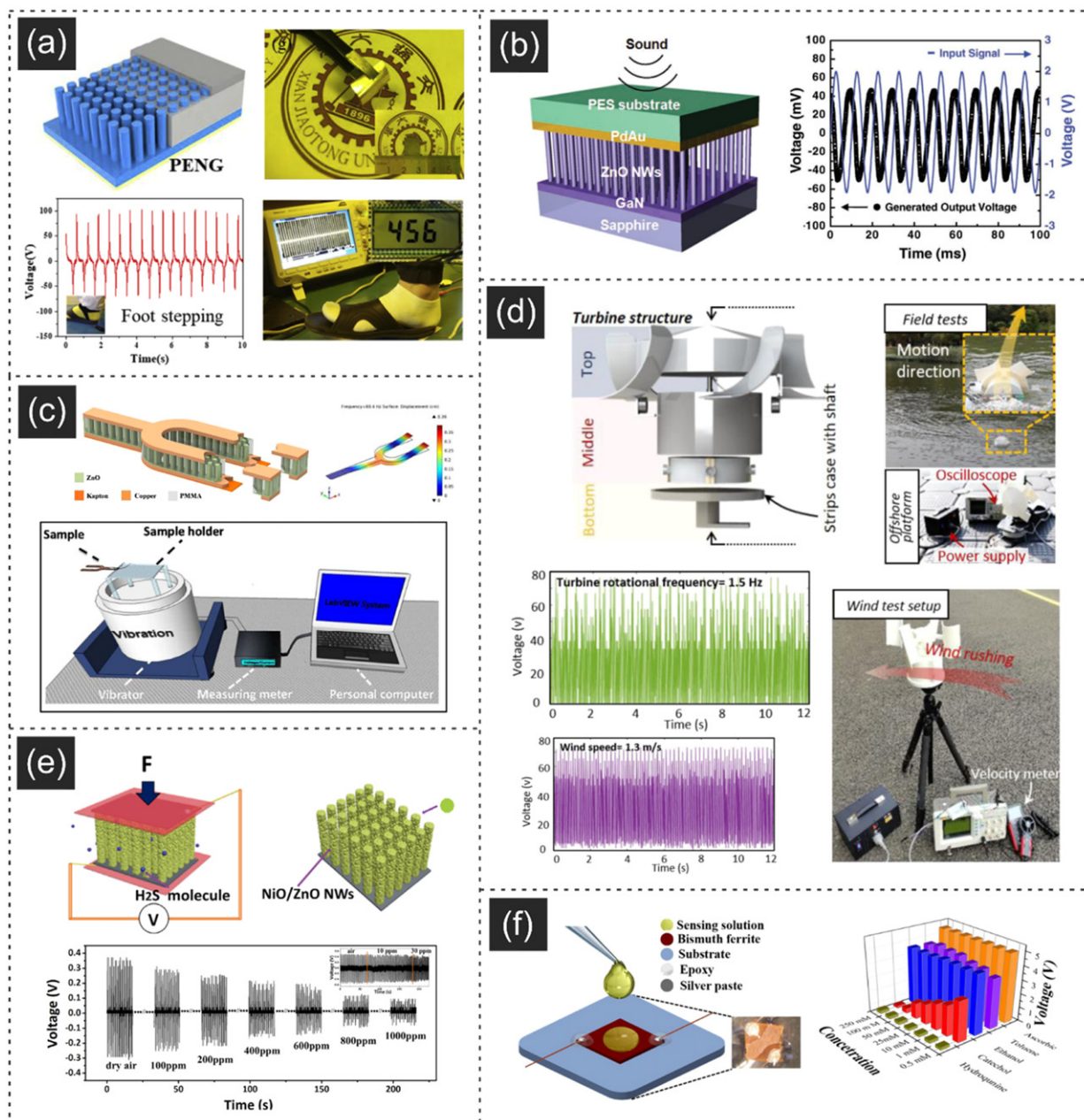


Fig. 20 Schematic illustration of surrounding energy harvesters and sensors using by PENG (a) PVDF-TrFE/BNNTs composite for general harvesting schemes, (b) ZnO NWs for sound wave scavenging, (c) fork-type ZnO NRs for low frequency vibrational harvesting, (d) PVDF-based turbine for multi-phases flow energy harvesting, (e) NiO/ZnO NWs arrays for a self-powered gas sensor, and (f) tube-shaped BiFeO₃ NPs for a self-powered chemical sensor. Reproduced from Ye, S., Cheng, C., Chen, X., *et al.*, 2019. High-performance piezoelectric nanogenerator based on microstructured P(VDF-TrFE)/BNNTs composite for energy harvesting and radiation protection in space. *Nano Energy* 60, 701–714. Cha, S.N., Seo, J.-S., Kim, S.M., *et al.*, 2010. Sound-driven piezoelectric nanowire-based nanogenerators. *Adv. Mater.* 22, 4726–4730. Deng, W., Jin, L., Chen, Y., *et al.*, 2018. An enhanced low-frequency vibration ZnO nanorod-based tuning fork piezoelectric nanogenerator. *Nanoscale* 10, 843–847. Egbe, K.-J. I., Matin Nazar, A., Jiao, P., *et al.*, 2021. Vibrational turbine piezoelectric nanogenerators for energy harvesting in multiphase flow fields. *Energy Rep.* 7, 6384–6393. Qu, Z., Fu, Y., Yu, B., *et al.*, 2016. High and fast H₂S response of NiO/ZnO nanowire nanogenerator as a self-powered gas sensor. *Sens. Actuators B: Chem.* 222, 78–86. Abisegapriyan, K.S., Maria Joseph Raj, N.P., Alluri, N.R., *et al.*, 2020. All in one transitional flow-based integrated self-powered catechol sensor using BiFeO₃ nanoparticles. *Sens. Actuators B: Chem.* 320, 128417.

depending on its concentration. This proposed PENG could generate peak-to-peak electrical outputs of ~ 16 V and ~ 30 nA upon external force directly applied to the device, with maximum power density of $2.62 \text{ mW} \cdot \text{m}^{-2}$ at $500 \text{ M}\Omega$. With regard to liquid flow sensing, the self-powered sensing unit could sense a small content of catechol down to $10.2 \mu\text{M}$, which is sufficient for detecting environmental contamination.

Self-Powered Active Sensors for Biomedical Applications

Energy harvesting systems applied *in vivo* and *in vitro* are promising candidates for self-powered medical devices (Yu *et al.*, 2021; Park *et al.*, 2017, 2018; Hwang *et al.*, 2014, 2015). A self-powered PENG used with the human body can harvest/sense biomedical energies from motions, muscle relaxation, cardiac pulse, respiration, and blood circulation, to name but a few (Yu *et al.*, 2021; Park *et al.*, 2017; Hwang *et al.*, 2014; Liu *et al.*, 2017). Fig. 21(a) shows an example of the use of PENG as a sensory system for human motion monitoring by Yu *et al.* (2021), focusing on a highly flexible $\text{BaTi}_{0.88}\text{Sn}_{0.12}\text{O}_3$ (BTS)-glass fiber fabrics (GFF)/PVDF composite films. The use of BTS with very low Curie temperature ($\sim 40^\circ\text{C}$) led to a high sensitivity when subjected to external force. The voltage and current sensitivities produced were approximately $1.23 \text{ V} \cdot \text{N}^{-1}$ and $41 \text{ nA} \cdot \text{N}^{-1}$, respectively. Additionally, this device could detect a very tiny force which is essential for broader monitoring applications. In sensing the arterial pulse on the epidermis, a conventional pressure sensor has core drawbacks of inelasticity and high power consumption. These shortcomings have been overcome by using a PENG-based self-powered pressure sensor. Park *et al.* (2017) demonstrated *in vivo* measurements of radial and carotid artery pulses near the epidermis, based on PZT thin films on ultrathin plastics, as shown in Fig. 21(b). The output voltage increased from 0.3 V to 1.85 V under input pressure ranging from 3.75 kPa to 25 kPa. The piezoelectric sensor enabled attachment to rugged skin throughout the body, thus allowing a fast response (0.018 kPa^{-1}) to tiny pulse signals. Also, the device could transmit pulse signals to a smart phone wirelessly *via* a microcontroller and Bluetooth electronic units. This work revealed the possibility of a self-powered and real-time healthcare sensor for long-term clinical diagnosis. Disabled people, who suffer from damaged or missing cochlear nerves, require a cochlear implantable device to aid their hearing. In this case, piezoelectric material can detect the sound pressure inside the fluid-filled cochlea, convert sound into electrical signals, and then stimulate the auditory neurons. As demonstrated by Park *et al.* (2018) in Fig. 21(c), the prototype PVDF-based intracochlear microphone has the potential for practical operation. Through the excellent characteristics of high elastic compliance, high environmental resistance and broadband frequency sensitivity (Choi *et al.*, 2017; Deng *et al.*, 2019), the selection of PVDF as an implantable microphone promoted sufficient signal-to-noise ratio ranging from 10 to 20 dB, effectively improving reception for the patients. Electrical signals from PENG can also be applied as a self-powered cardiac pacemaker for regulating heartbeats for patients who suffer from sick sinus syndrome or heart block, which affects their normal heart rate (Hwang *et al.*, 2014; Kumar *et al.*, 2018). These PENG-based cardiac pacemaker do not require a conventional battery or lengthy/time-consuming maintenance. Hwang *et al.* (2014) selected the single crystalline $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$ (PMN-PT) thin film to achieve a self-powered artificial pacemaker (Fig. 21(d)). With an outstanding piezoelectric charge constant (d_{33} of $2500 \text{ pC} \cdot \text{N}^{-1}$), the PMN-PT based PENG generated the highest output voltage and current of $\sim 8.2 \text{ V}$ and $\sim 145 \mu\text{A}$, respectively, by continuous bending motion. The latter task clearly demonstrated the potential of a flexible harvester for recharging batteries and electrically simulating the heartbeat of a living rat. In addition, the interfacing application with PENG is of interest not only for heart but also deep brain stimulation. Deep brain stimulation is a kind of neurosurgical process using electrical signals to stimulate the brain in a specific area, which enables effective treatments for various symptoms, *e.g.*, Parkinson's disease, essential tremor, dystonia, Tourette syndrome, *etc.*, (Perlmutter and Mink, 2006; Lee *et al.*, 2019a). The implantable brain stimulator normally requires surgery to replace a battery with short lifetime. It is thus desirable to utilize PENG as a self-powered device for brain stimulation. Hwang *et al.* (2015) also adopted the $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3 - \text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - \text{PbTiO}_3$ (PIMNT) thin film, which had excellent d_{33} of up to $\sim 2700 \text{ pC} \cdot \text{N}^{-1}$ in bulk structure (Fig. 21(e)). Using a PIMNT based PENG could produce extreme maximum output voltage and output current of 11 V and 0.57 mA, respectively, from mechanical deformation. The energy harvesting device could activate a specific neuron to induce the body movements of a mouse. This concept eliminates implantable devices that use a battery for the power supply, opening up the route for future development of neuroscience in medical treatment technology.

Self-Powered Active Sensors for Smart Electronics

A PENG-based self-powered system is desirable for diverse smart sensing technologies, wearable electronics, IoT, artificial intelligence (AI), virtual reality (VR), augmented reality (AR), and human-machine interface, and so on (Kim *et al.*, 2018a; Song *et al.*, 2019; Zhang *et al.*, 2015a; Yang *et al.*, 2020). Owing to its ability to convert mechanical energy into an electrical signal, PENG can not only drive various sensing parts efficiently, but also sense and transmit signals to a receiver without an external power supply, as it is a self-powered device.

In recent years, many PENG-based active sensors for smart electronic applications have been reported (Rana *et al.*, 2020; Wang *et al.*, 2015; Lu *et al.*, 2020; Han *et al.*, 2018). For a full wireless sensing system, Rana *et al.* (2020) used a porous PVDF-based PENG to deploy a built-in sensor network. The fabricated device provided ~ 8 and ~ 11 times enhancement of output voltage and current, respectively, when compared with a pristine PVDF PENG. The proposed PENG demonstrated potential for being a self-powered structural health monitoring device by remote sensing networks, as shown in Fig. 22(a). The rise of IoT technology relates to the large-scale constructions of various sensing nodes, and the receiver that displays the analyzed signals. In general, most sensors require an external power supply for operation, which is well suit for the replacement by PENG. Kim *et al.* (2018a) used a novel piezoelectric system of $0.72\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3 - 0.28\text{Pb}[(\text{Zn}_{0.45}\text{Ni}_{0.55})_{1/3}\text{Nb}_{2/3}]\text{O}_3$ doped with CuO (PZNC) to produce a piezoelectric floor tile for mechanical energy harvesting. This composition provided a high piezoelectric coefficient, due to the vicinity of the rhombohedral-tetragonal morphotropic phase boundary. When fabricated into a floor tile, the peak output voltage and current reached 42 V and 52 μA , respectively, upon each step by a person. It was possible to wirelessly transmit a signal from a footstep and trigger the receiver node of a main electrical appliance in a smart home (Fig. 22(b)). In recent times, the electronic signature has been used widely for remote communication during the Covid-19 pandemic. However, the current technology

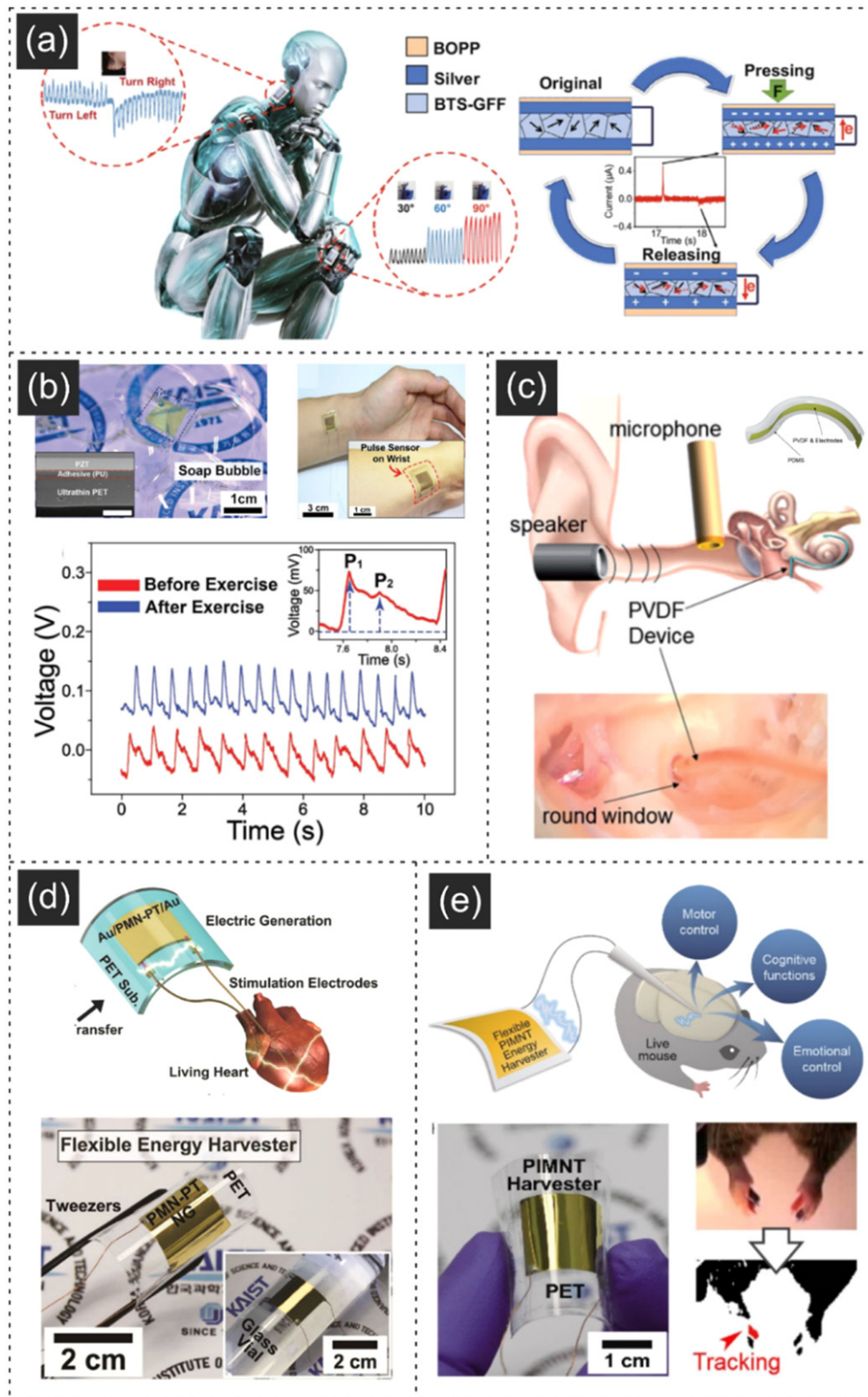


Fig. 21 Schematic illustration of *in vitro* and *in vivo* biomedical electronics using PENG (a) BTS films deposited on glass fiber fabrics for human gesture monitoring, (b) a wearable PZT-based piezoelectric pulse sensor, (c) PVDF-based piezoelectric microphone for sound detection inside gerbil and human cochleae, (d) PMN-PT thin film on a plastic substrate for a self-powered artificial cardiac pacemaker, and (e) PIMNT thin film on a plastic substrate for self-powered deep brain stimulation. Reproduced from Yu, D., Zheng, Z., Liu, J., *et al.*, 2021. Superflexible and lead-free piezoelectric nanogenerator as a highly sensitive self-powered sensor for human motion monitoring. *Nano-Micro Lett.* 13, 117. Park, D.Y., Joe, D.J., Kim, D.H., *et al.*, 2017. Self-powered real-time arterial pulse monitoring using ultrathin epidermal piezoelectric sensors. *Adv. Mater.* 29, 1702308. Park, S., Guan, X., Kim, Y., *et al.*, 2018. PVDF-based piezoelectric microphone for sound detection inside the cochlea: Toward totally implantable cochlear implants. *Trends Hear.* 22, 2331216518774450. Hwang, G.-T., Park, H., Lee, J.-H., *et al.*, 2014. Self-powered cardiac pacemaker enabled by flexible single crystalline PMN-PT piezoelectric energy harvester. *Adv. Mater.* 26, 4880–4887. Hwang, G.-T., Kim, Y., Lee, J.-H., *et al.*, 2015. Self-powered deep brain stimulation via a flexible PIMNT energy harvester. *Energy Environ. Sci.* 8, 2677–2684.

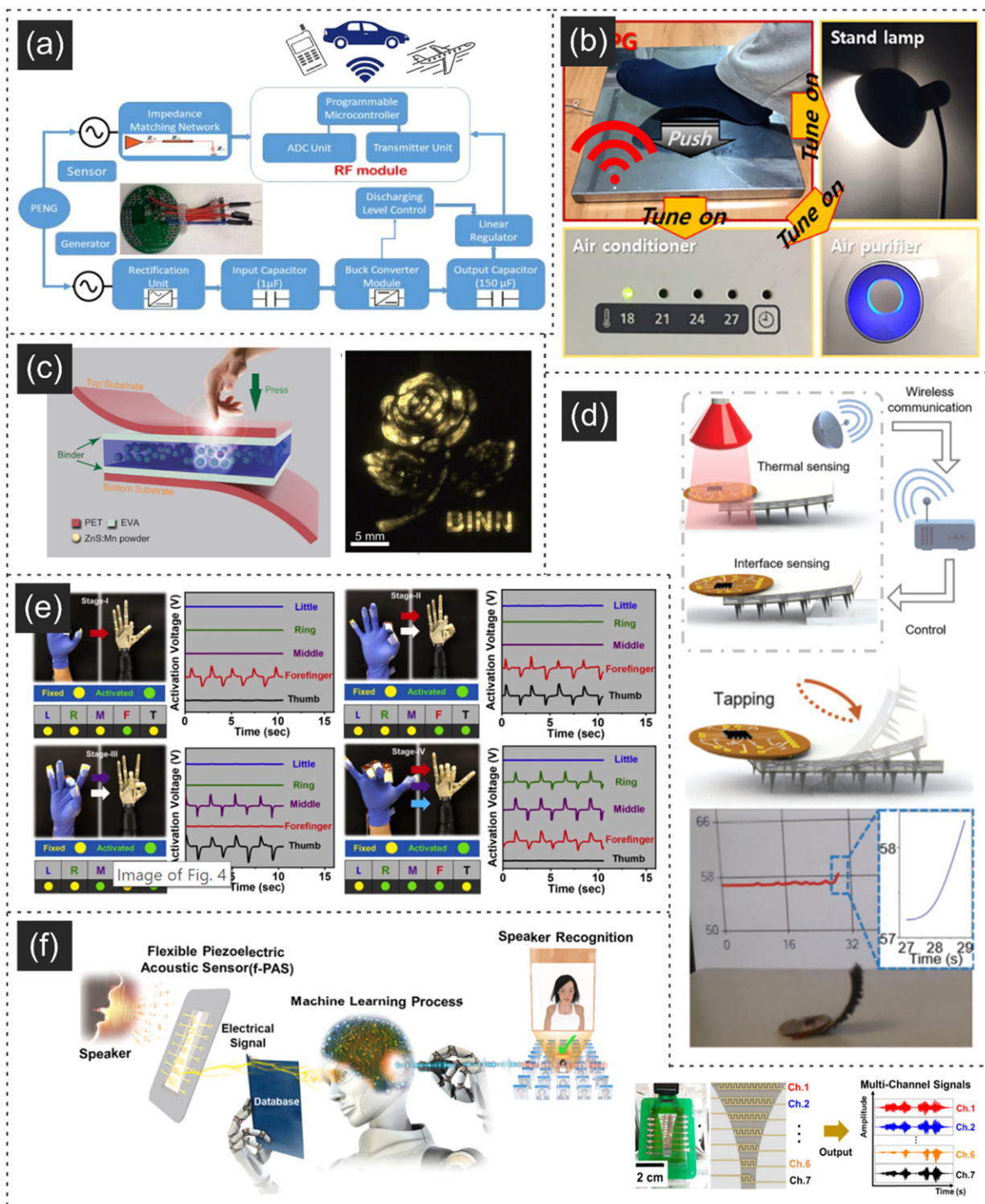


Fig. 22 Schematic illustration of smart electronics using PENG (a) porous PVDF-based film, demonstrating feasibility of a wireless sensing system, (b) PZNC film built as a smart floor tile for home energy management, (c) mechanoluminescent ZnS:Mn particles sandwiched between two polymeric layers for visualized 2D planar pressure mapping, (d) PZT/PDMS composite for a battery-less soft millirobot with battery-less sensing system, (e) SnS₂ NSs deposited on polyimide substrate for the synchronous human-robot interface, and (f) PZT thin film for a speech recognition system. Reproduced from Rana, M.M., Khan, A.A., Huang, G., *et al.*, 2020. Porosity modulated high-performance piezoelectric nanogenerator based on organic/inorganic nanomaterials for self-powered structural health monitoring. *ACS Appl. Mater. Interfaces* 12, 47503–47512. Kim, K.-B., Cho, J.Y., Jabbar, H., *et al.*, 2018a. Optimized composite piezoelectric energy harvesting floor tile for smart home energy management. *Energy Convers. Manag.* 171, 31–37. Wang, X., Zhang, H., Yu, R., *et al.*, 2015. Dynamic pressure mapping of personalized handwriting by a flexible sensor matrix based on the mechanoluminescence process. *Adv. Mater.* 27, 2324–2331. Lu, H., Hong, Y., Yang, Y., *et al.*, 2020. Battery-less soft millirobot that can move, sense, and communicate remotely by coupling the magnetic and piezoelectric effects. *Adv. Sci.* 7, 2000069. Yang, P.-K., Chou, S.-A., Hsu, C.-H., *et al.*, 2020. Tin disulfide piezoelectric nanogenerators for biomechanical energy harvesting and intelligent human-robot interface applications. *Nano Energy* 75, 104879. Han, J.H., Bae, K.M., Hong, S.K., *et al.*, 2018. Machine learning-based self-powered acoustic sensor for speaker recognition. *Nano Energy* 53, 658–665.

cannot record essential information for the signees, *e.g.*, intensity of pressure applied and speed of writing, which are secured personally. Implementation is achieved by using PENG as demonstrated by Wang *et al.* (2015). Their proposed work utilized ZnS: Mn particles as mechanoluminescent materials sandwiched between two polymeric layers for dynamic 2D mapping of the input pressure (Fig. 22(c)). The working mechanism is believed to be the coupling effect between piezoelectricity and photoexcitation processes, which is a result of handwriting-induced visible light emission. The secure signature system is achieved by collecting the signing habits from different signees. This system gives unique and reliable personalized information that can fulfill a high-level security technology. Soft millirobot development is also a promising candidate for biomedical treatments such as drug delivery and targeted diagnosis (Patra *et al.*, 2018; Hu *et al.*, 2020). Due to the small size of the robot, there are still the challenges of power supply, management, electronic integration and working in a harsh environment. To overcome these issues, Lu *et al.* (2020) designed a battery-less soft millirobot, which was able to sense, move and communicate remotely based on the coupling of magnetic and piezoelectric effects, as shown in Fig. 22(d). Its structural design consisted of electronic circuits (actuation and communication functions) in a multilayer thin film connected to multiple tapered feet. A constructed PZT foam layer provided piezoelectric energy harvesting which communicates the electrical response to the microcontroller unit (MCU). Under the trigger of an external magnetic field, the proposed robot could move, environmentally sense, and wirelessly transmit data without the need of an external power supply. This concept is thus useful for a broad spectrum of promising applications such as *in vivo* biomedical diagnosis and space. Human-machine interface relates to the interactive control between person and machine *via* a computer/smartphone based graphical user interface. The piezoelectric device can be employed for driving synchronous human-machine interaction. Yang *et al.* (2020) selected tin disulfide nanosheets (SnS₂ NSs) due to their excellent electron mobility, high chemical stability, and existence of piezoelectric effect (Alyörük *et al.*, 2015). The as-synthesized SnS₂ NSs were fabricated as a flexible PENG for biomedical energy harvesting and sensing. It generated an output voltage and output current of ~6 mV and ~60 pA, respectively, under the strain of 0.44%. Also, the self-powered SnS₂ NSs-based PENG successfully demonstrated the intelligent human-robotic interface for the smart sign language system (Fig. 22(e)). This finding opens a new route to the development of sensing technology with advanced 2D NSs-based devices beyond SnS₂ NSs. Voice recognition is a technology that allows the user to communicate with and control smart devices based on machine learning, AI, and IoT systems (Johnson *et al.*, 2014). In a general voice recognition process, the incoming sound wave is detected by a condenser microphone. A conventional microphone has distinctive issues of low sensitivity, large size, complex framework, and high-power consumption rate. Therefore, Han *et al.* (2018) developed a machine learning-based speaker recognition system based on a self-powered flexible piezoelectric acoustic sensor (Fig. 22(f)). PZT layers were spin-coated onto a multi-channel dashboard. A concaved trapezoidal design was utilized to identify multiple piezoelectric voice signals. Machine learning strategy enabled signal analysis to produce an outstanding speaker recognition rate of 97.5% with very low error rate. This achievement is appropriate for development in voice-based biometric authentication, which is highly essential for future security technology.

Concluding Remarks and Future Prospects

This article firstly introduced the background and significance of energy harvesting by using the piezoelectric effect. The second topic presented the fundamental theory of the origin of piezoelectricity. Comprehensive reviews on working mechanisms in different force directions, mathematical formulation that explained the conversion process, essential figures of merit, and structural modeling including a representative operation box and theoretical simulation of the PENG were presented. The third topic pointed out the generations of piezoelectric material development. Three generations of piezoelectric materials comprise of piezoelectric oxide nanostructure, synthetic piezoelectric polymers and composites, and organic piezoelectric materials and composites. Examples of PENG structural designs were discussed in detail in the fourth section. The final topic reviewed the literature to demonstrate the potential for practical applications, such as general energy harvesting and sensing from an ambient environment, self-powered active sensors for medical monitoring and treatment, and self-powered active sensors for emerging electronics.

In recent years, smart applications technologies have emerged continuously, *e.g.*, IoT, big data, VR, AR, robotic control, and human-machine interaction. Consequently, the commercialization of self-powered devices is more focused on supporting these technologies. Even though the piezoelectric effect has been discovered and studied for a long time, there is still room for research development in every application, due to the unique characteristics of piezoelectric-based devices. For example, piezoelectric materials were used in the past for vibrational energy scavenging based on the unimorph and bimorph cantilever (Lin *et al.*, 2009; Yi *et al.*, 2002; Erturk and Inman, 2009). Also, piezoelectric ceramics were built on a large-scale for simple impact energy harvesting and sensing (Kim *et al.*, 2018a; Puscasu *et al.*, 2018). The conventional use of piezoelectric materials was normally in the form of rigid, inorganic materials such as ceramics-based BT and PZT. However, with the current need for flexible, transparent and lightweight materials for flexible electronics, piezo-materials have been developed in the form of polymeric composites to overcome these limitations (Charoonsuk *et al.*, 2019; Huan *et al.*, 2018). This concept is an attractive approach because of high flexibility of the material and structural designs. Moreover, some organic materials such as cellulose (Wu *et al.*, 2021; Chen *et al.*, 2021), chitosan (Hosseini *et al.*, 2020; Pongampai *et al.*, 2021) and polylactic acid (Hanani *et al.*, 2021), can be used as efficient bio-piezoelectric materials by combining with functional nanophases. Through this strategy, the emerging bio-PENG has been evoked, with its excellent properties of biocompatibility, biodegradability, stretchability, portability, and low-cost. It is highly suitable for use with patients in diverse medical technologies, with the potential to reduce toxic e-wastes in the near future.

It is important to note that before its practical use and distribution in the marketplace, development of the piezoelectric energy harvester has to meet many challenges as follows:

Performance

PENG generally produces low (<100 V) electrical outputs. Also, due to the large internal impedance, PENG conventionally provides very low output current in nano- to micro-ampere ranges. While this is sufficient for sensing, the improvement is required for effective energy harvesting. This includes making the composite with functional nanomaterials (Charoonsuk *et al.*, 2019; Huan *et al.*, 2018; Sriphan *et al.*, 2019), chemical doping (Liu *et al.*, 2016a; Lee *et al.*, 2013), alignment of piezoelectric NFs (Anand and Bhatnagar, 2019; Yan and Jeong, 2016), bilayer structures (Liu *et al.*, 2014; Yaqoob *et al.*, 2017), and surface treatments (Hussain *et al.*, 2014; Jalali *et al.*, 2014). In addition, novel structural designs (Wu *et al.*, 2018; Su *et al.*, 2021; Puscasu *et al.*, 2018) are simple methods that have potential for practical uses.

Device Integration

The piezoelectric-based device has a limitation in harvesting only mechanical energy. For future sustainable applications, PENG should be integrated with other harvesting technologies in order to build hybrid systems, for instance, triboelectricity (Sriphan *et al.*, 2019; Sriphan *et al.*, 2020; Pongampai *et al.*, 2021; Charoonsuk *et al.*, 2021), solar cell (Rahman and Chakravarty, 2019), electromagnetic field (Bolat *et al.*, 2019; Qi *et al.*, 2021), thermoelectric cell (Montgomery *et al.*, 2016), and pyroelectric cell (You *et al.*, 2018). Such integration will not only improve the output performance but also assist in the development of multi-energy harvesting units. However, it has been noticed that combining harvesting technologies together with different mechanisms in one structure might lead to negative performance, especially considering simultaneously incoming energies in different phases and frequencies. Furthermore, PENG can be built to achieve an intelligent system with machine learning and wireless control. Integrating with other sensing modules also is possible, but one needs to carefully design electronic systems to provide low power consumption, low noise, stable operation, and capability of storing data and energy.

Industrial Fabrication and the Market

Nowadays, piezoelectric-based devices (both flexible and inflexible) can be easily found in the e-market at low-price. PZT is the widely used piezoelectric material because of its excellent piezoelectric properties. Due to toxicity, however, another lead-free piezoelectric material, *i.e.*, BT, has been selected (Liu and Ren, 2009). Unfortunately, the conversion performance of the device based on these inorganic oxides is still low for practical applications. Moreover, piezoelectric composite can be prepared by coupling between piezoelectric nanofiller and the polymeric host to gain more performance, flexibility, lightweightness and easy practical design (Huan *et al.*, 2018; Ye *et al.*, 2019; Sriphan *et al.*, 2019; Lu *et al.*, 2021). However, reliable large-scale preparation is rather difficult due to the complex system, in addition to the lengthy preparation and high fabrication cost. Hence, reliable preparation techniques that support rapid and mass production are still in great need for diverse forms of materials and incoming smart applications. Even though the PZT-based piezoelectric harvester has been spread widely in the market, the core application is rather narrow, which focuses mostly on the scavenge of simple impact force and vibrational energy. To expand to novel applications such as wearable electronics, more consideration of factors such as flexibility, portability, comfortability, biocompatibility and freedom from toxicity, should be given. Full structural design is also significant. Long-term operation of PENG with exposure to air, light and dust causes the device to degrade. Thus, packaging technology is essential to improve stability and durability by protecting the device from the deteriorating environment (Zhou *et al.*, 2021; Lu *et al.*, 2021; Kim *et al.*, 2018d).

Profits from piezoelectric products mainly depends on market demand and satisfaction of the customer as well as cost-effectiveness. It is believed that piezoelectric-based devices are not obsolete, even though harvesting and sensing technologies have changed rapidly. From that viewpoint, researchers should continuously develop PENG to cover the structural design, material, device performance, and fabrication method. Quality, standard and stability should not be overlooked in marketing strategies.

Declaration of Competing Interest

The authors declare no known competing financial interests or personal relationships that could influence the work reported in this paper.

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Bulk and Thin Film TE Materials and Applications

Tosawat Seetawan and Athorn Vora-ud, Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Sakon Nakhon, Thailand

Kunchit Singsoog and Wanatchaporn Namhongsa, Center of Excellence on Alternative Energy, Sakon Nakhon Rajabhat University, Sakon Nakhon, Thailand

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Abstract

We prepared nano-powder precursors by a planetary ball mill method. We synthesized the bulk thermoelectric (TE) by hot-pressing method and multi-magnetron sputtering method for the film TE. A couple of bulk TE shows electrical power in milliwatts order and microwatts for the film. We applied the bulk & film TE devices within harvesting energy for nano and microsensors, small charging systems, and personal cooling systems depending on low temperature, medium temperature, and high-temperature applications of heat side or different temperatures. In addition, we have agreed to collaborate with Thai Thermoelectric Society (TTS), Asia Associate Thermoelectric (AAT), and TE companies to simulate, synthesize, fabricate, and infrastructure TE equipment. We have TE applications such as microgenerators, personal temperature control, helmet temperature control, heat pump, and thermoelectric air conditioner.

Key Points

- Synthesis
- Characterization
- Fabrication
- Applications of Bulk and Thin Film Thermoelectric Materials and Devices.

Introduction

The energy needs to be available and affordable to all to allow future development, and it needs to be clean to ensure that the development can be sustainable. The Sustainable Development Goals (SDGs) no.7 is affordable and clean energy. Thermoelectric energy is recognizable in the performance of work and in the form of heat and electric. TE technology is solid-state heat pumps and renewable energy that support everyone life which directly converts heat into electricity and vice versa, with no moving parts, and is environmentally friendly. TE promotion is solid state construction (no moving parts), diffusion barriers, vibration-free operation, no acoustical or electrical noise, size and performance output highly scalable of 2–60 mm, fully scalable mW to kW of heat pumping or power output depending on design, long lifetime, free of maintenance, direct conversion, power from waste heat, refrigeration without freon gas, green energy production, automobile waste heat TE power generation and on-chip TE cooling. TE efficiency depends on the dimensionless figure of merit (ZT). We need to high electrical conductivity and Seebeck coefficient but low thermal conductivity. TE materials included bulks, thin films, nanoparticles, superlattices, nanocomposites, nanowires, and quantum dots. TE research and development are a fabrication of nanostructures, robust TE, characterization, higher reliability, better structural stability, efficient TE modules, bulk and low-cost production, better simulation, and analysis tools. TE potential markets are a consumer (35%), automobile (14%), telecom (16%), medical and bio (12%), industry (9%), semiconductor process (8%), and defense & space (6%).

Background/Fundamentals

TE materials show converting heat energy into electricity, and great potential in waste heat utilization and energy storage. The TE performance is specified $ZT = S^2T/\rho\kappa$, where S is the Seebeck coefficient, T is the absolute temperature, ρ is the electrical resistivity, and κ is the total thermal conductivity (Aswal *et al.*, 2016). High-performance TE materials have a significant Seebeck coefficient, low thermal conductivity like a phonon-glass concept, and high electrical conductivity like an electron-crystal concept (Rahman *et al.*, 2019). However, the non-toxic elements, widely available in nature and preferably as lightweight as possible for applications. For example, automobiles, have qualified to fabricate TE materials. Nowadays, several TE materials have been recently developed, such as oxide, (Zhang *et al.*, 2019) tellurite, (Ahmad *et al.*, 2019) half Heusler, (Du *et al.*, 2019) chalcogenide, (Sharma *et al.*, 2018; Dahshan *et al.*, 2017) and silicide (Pham *et al.*, 2019). Among them, silicide-based materials are considered the best candidate for mid to high-temperature TE applications (673–873K) as their constituents are highly abundant, inexpensive, non-toxic, and maintain high stability (Ivanova, 2011). Since the 1990s, oxide TE materials have been considered promising TE materials because of their non-toxicity, low cost, and chemical stability at high temperatures. The studied results show great potential for applications in TE power generators at high temperatures and have thus drawn attention over the years, but the modules' performance is still relatively low, especially compared to

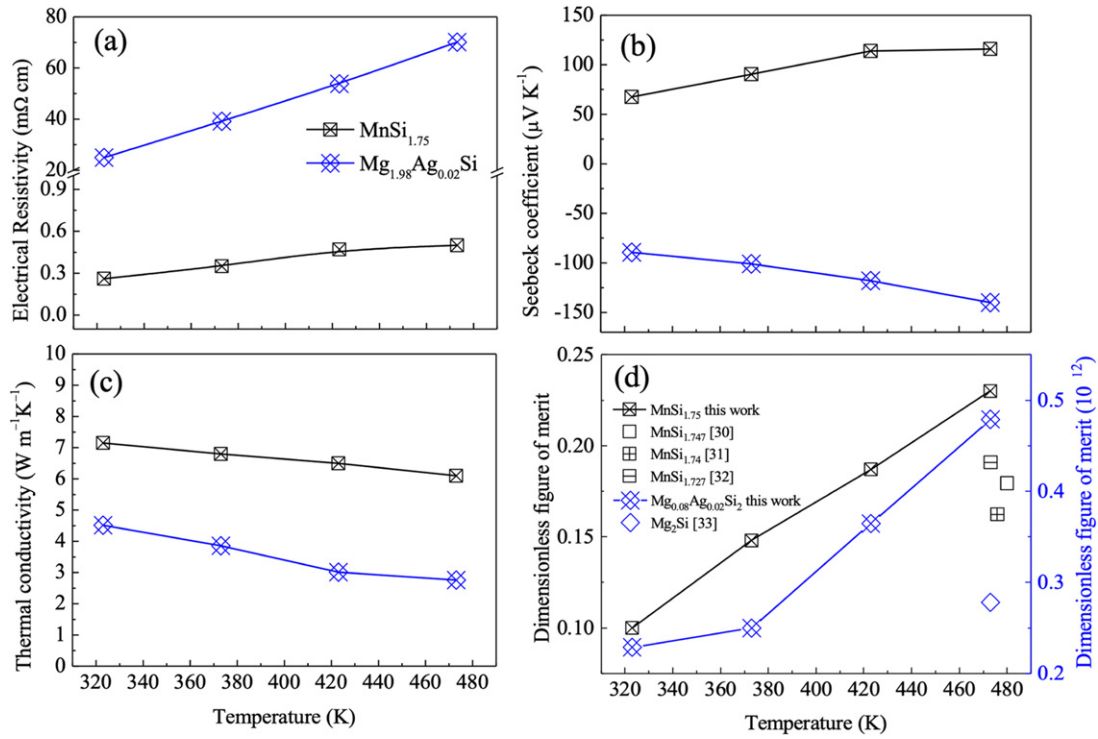


Fig. 1 The TE properties dependence on temperature of p-MnSi_{1.75} and n-Mg_{1.98}Ag_{0.02}Si (a) electrical resistivity, (b) Seebeck coefficient, (c) thermal conductivity and (d) dimensionless figure of merit.

non-oxide materials (Ohtaki, 2011; Pryds and Rasmus, 2020; Funahashi, 2021). Among TE oxide materials, *p*-type layered cobaltite Ca₃Co₄O₉ (CCO) and *n*-type perovskite CaMnO₃ (CMO) have been intensively investigated and considered promising candidates for high-temperature applications. For *p*-CCO with values of *ZT* up to 0.40 at 975 K, (Yin *et al.*, 2010) *n*-CMO materials still need to be further studied because they do not have *ZT* values as good as *p*-type materials. Studies on CMOs presented in the literature obtained *ZT* values in the range of 0.018–0.075 (Torres *et al.*, 2020). In this work, we have synthesized the *p*-CCO/*n*-CMO by using the solid-state reaction method and the hot-pressed method. The telluride-base TE material system provides the best TE performance at room temperature (Shang *et al.*, 2020). Improving the *ZT* requires reducing the thermal conductivity and controlling the transport of phonons and electrons within the thin-film superlattices (Liu *et al.*, 2016; Tang *et al.*, 2007; Zhao *et al.*, 2005). In this present, *p*-type (Sb-Te; *p*-ST) and *n*-type (Bi-Te; *n*-BT) thin films were enhanced of TE properties to be fabricated of thin film TE module by using the DC magnetron sputtering method.

Bulk TE Materials

p-MnSi_{1.75}/n-Mg_{1.98}Ag_{0.02}Si Bulk TE Materials

Electrical properties

The electrical resistivity dependence on temperature of MnSi_{1.75} and Mg_{1.98}Ag_{0.02}Si materials are shown in Fig. 1(a). Both materials show an inverse relationship, i.e., a slightly decreasing electrical resistivity dependence with increasing temperature. This relationship indicates a degenerative semiconducting behavior (Singsoog and Seetawan, 2019). The Mg_{1.98}Ag_{0.02}Si shows a value of electrical resistivity of about 70.12 mΩ cm at 473 K, which is lower than Mg₂Si non-doped (88.99 mΩ cm), (Shin *et al.*, 2013) hence Ag doped can increase the carrier concentration (Hilaal Alama and Ramakrishna, 2013a). The electrical resistivity can be derived by Eq. (1) and Eq. (2) (Tang *et al.*, 2016).

$$\rho = \frac{1}{\sigma} = \frac{1}{ne\mu} \quad (1)$$

where μ is the carrier mobility, n is the carrier concentration, e is the electron charge, and σ its electrical conductivity.

$$\sigma = \frac{A}{T} \exp\left(\frac{-E_a}{k_B T}\right) \quad (2)$$

where A is the pre-exponential factor, k_B is Boltzmann's constant (1.38×10^{-23} J/K), T the absolute temperature, and E_a the activation energy of conduction.

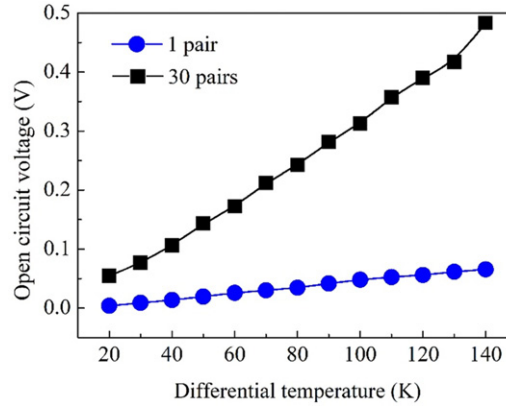


Fig. 2 Open circuit voltage dependence on different temperature of TE devices.

The Seebeck coefficient of $\text{MnSi}_{1.75}$ and $\text{Mg}_{1.98}\text{Ag}_{0.02}\text{Si}$ shows positive and negative values indicating p-type (Hilaal Alama and Ramakrishna, 2013b) and n-type (Tani and Kido, 2005) thermoelectric materials, respectively. The absolute Seebeck coefficient of both materials increased with increasing temperature, which is typical metallic diffusion behavior (Sivakumar *et al.*, 2006). The maximum Seebeck coefficient value of $\text{MnSi}_{1.75}$ and $\text{Mg}_{1.98}\text{Ag}_{0.02}\text{Si}$ are $116 \mu\text{V K}^{-1}$ and $-140 \mu\text{V K}^{-1}$ at 473 K, respectively, as shown in Fig. 1(b). The Seebeck coefficient is derived following Eq. (3).

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{\frac{3}{2}} \quad (3)$$

where h is Planck's constant ($6.62 \times 10^{-34} \text{ J s}$), m^* is the effective carrier mass ($m^* = N_V^{2/3} m_b^*$, where N_V is the number of conduction bands and m_b^* is the effective band mass).

Thermal properties

The thermal conductivity of $\text{MnSi}_{1.75}$ and $\text{Mg}_{1.98}\text{Ag}_{0.02}\text{Si}$ materials decreased with increasing temperature, as shown in Fig. 1(c). Both materials' total thermal conductivity values are $6.1 \text{ W m}^{-1} \text{ K}^{-1}$ and $2.76 \text{ W m}^{-1} \text{ K}^{-1}$ at 473 K, respectively. The total thermal conductivity can be evaluated by Eq. (4) (Ohtaki, 2010).

$$\kappa_{\text{tot}} = \kappa_{\text{el}} + \kappa_{\text{ph}} \quad (4)$$

The Wiedemann-Franz relationship illustrates electronic thermal conductivity (κ_{el}) (Fergus, 2012).

$$\kappa_{\text{el}} = L\sigma T \quad (5)$$

$$\frac{\kappa_{\text{el}}}{\sigma} = \left(\frac{\pi^2 k_B^2}{3e^2} \right) T \quad (6)$$

where L is Lorenz constant ($2.45 \times 10^{-8} \text{ W K}^{-2}$). The lattice thermal conductivity (κ_{ph}) can be calculated from the classical kinetic theory, as shown in Eq. (7) (Sootsman *et al.*, 2009).

$$\kappa_{\text{ph}} = \frac{1}{3} C_V v l_{\text{ph}} \quad (7)$$

where C_V is the specific heat at constant volume, l_{ph} is the mean free path, and v is the average sound velocity ($v = \sqrt{\gamma \cdot \frac{p}{\rho}}$ where γ is the adiabatic index, p is the pressure, and ρ is the density). In this experiment, we used the steady-state method for measuring thermal conductivity, followed by Eq. (8) and Eq. (9).

$$\kappa = \frac{\dot{Q}l}{A\Delta T} \quad (8)$$

$$\dot{Q} = Q_{\text{in}} - Q_{\text{loss}} \quad (9)$$

where $\dot{Q}$ is the amount of heat flowing through the sample, A is the cross-sectional area of the sample, l and ΔT are the distance and temperature difference between temperature sensors, Q_{in} is the applied heating power at the heat source side, and Q_{loss} are the parasitic heat losses due to radiation, conduction, and convection to the ambient temperature (Zhao *et al.*, 2016). The ZT of materials were calculated from TE properties including S , ρ and κ . The ZT of $\text{p-MnSi}_{1.75}$ and $\text{n-Mg}_{1.98}\text{Ag}_{0.02}\text{Si}$ materials compared with literature data (Homma *et al.*, 2019; Salvoa *et al.*, 2019; Lee *et al.*, 2017; Fiameni *et al.*, 2012) dependence on temperature increased with increasing temperature, as shown in Fig. 1(d). The $\text{p-MnSi}_{1.75}$ shows a high ZT value of about 0.23 at 473 K, and $\text{n-Mg}_{1.98}\text{Ag}_{0.02}\text{Si}$ shows a maximum ZT value of about 0.47×10^{-2} at 473 K, hence the ZT value of $\text{MnSi}_{1.75}$ is approximately 49 times higher than that of $\text{Mg}_{1.98}\text{Ag}_{0.02}\text{Si}$.

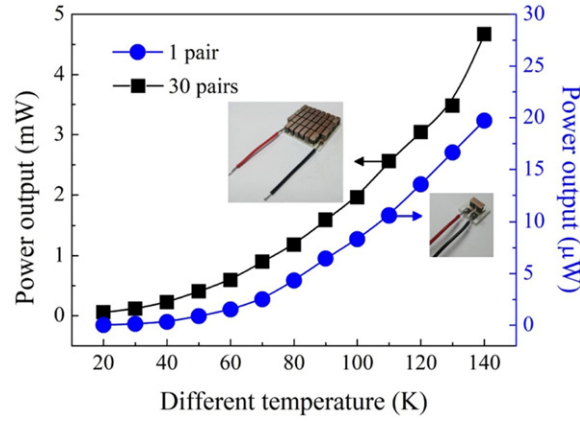


Fig. 3 Power output dependence on different temperature of TE devices.

p-MnSi_{1.75}/*n*-Mg_{1.98}Ag_{0.02}Si bulk power generation

Open circuit voltage dependence with different temperatures of 1 pair and 30 pairs TE devices are shown in Fig. 2. Both devices show an increasing open circuit voltage with increasing temperature and maximum values of about 65.60 mV and 483.30 mV, respectively, at different temperatures of 140K. The power output of 1 pair and 30 pairs of TE devices dependent on different temperatures is shown in Fig. 3. The power output was measured by matching load 2 for 1 pair (resistance is 2.2) and 50 for a module (resistance is 55). The power output of TE devices increased with increasing temperature. The maximum power output values of both devices are 19.72 μW and 4.67 mW at a different temperature of 140K, respectively, hence the power output for the 30 pairs is approximately 237 times more significant compared to the 1 pair device. Because the materials are connected with good contact, confirmed by SEM micrograph, the theoretical conversion efficiency can be derived by Eq. (10).

$$\eta = \frac{W}{Q_H} = \frac{I[(S_p - S_n)\Delta T - IR]}{K\Delta T + (S_p - S_n)IT_H - \frac{1}{2}I^2R} \quad (10)$$

In which the Seebeck coefficient of *n*-Mg_{1.98}Ag_{0.02}Si (S_n) is larger than the Seebeck coefficient of *p*-MnSi_{1.75} (S_p), and thermal conductance (K) of both types are high value. However, we obtained the electrical power from 1 pair and 30 pairs in order milliwatt.

p-CCO/*n*-CMO Bulk TE Materials

For both S , it was found that the ceramic showed semiconductor behavior upon increasing the temperature. The signs of *Sp*-CCO and *n*-CMO are positive and negative, respectively. In the horizontal shape *p*-CCO/Ag/*n*-CMO, the S values were between the values of two single components. The intrinsic S value of the horizontal leg can be expressed via single components as (Apertet et al., 2015):

$$S_{||} = \frac{\Delta V}{\Delta T} = \frac{\kappa_{CCO}S_{CCO} + \kappa_{CMO}S_{CMO}}{\kappa_{CCO} + \kappa_{CMO}} \quad (11)$$

where $S_{||}$ is the Seebeck coefficient of the horizontal shape *p*-CCO/*n*-CMO leg, κ_{CCO} , S_{CCO} , are thermal conductivity, Seebeck coefficient of *p*-CCO ceramics, κ_{CMO} , S_{CMO} thermal conductivity and Seebeck coefficient of *n*-CMO, respectively.

The temperature dependence of the TE properties of the single *p*-CCO and single *n*-CMO is shown in Fig. 4.

p-CCO/*n*-CMO bulk TE devices

TE modules are traditionally assembled from tens or hundreds of TE couples arranged electrically in series, thermally in parallel, and fitted into a planar enclosure. The TE couple is composed of *p*- and *n*-type semiconductors. The elements of a TE couple and the TE couples are separated by gaps determined by the module fill factor, denoted as the ratio of the area occupied by elements to the area of the module base. These external gaps can lead to heat loss between the heat source and sink and, consequently, lower the temperature difference between the hot and cold junctions of the TE couples. Previously, the fabrication and power generation of oxide TE modules had a low conversion efficiency. However, they were composed of non-toxic, commonly accessible elements with good chemical stability in the air, even at temperatures as high as 800–1000K. For example, a *p*-Ca₃Co₄O₉, *n*-Ca_{0.97}Bi_{0.03}MnO₃ was reported by Paengson (2016). It was found that the π -shape had the highest maximum voltage of 76.8 mV, with an electrical current of around 70 mA. Electrical power of 4 mW at a temperature difference of 200 K. A TE module based on ΔT a low of 12 pairs of *p*-CCO/*n*-CMO legs with novelty dimensions of $0.5 \times 5 \times 3 \text{ mm}^3$ was fabricated using a low cost of Cu electrodes and ceramic substrates. With a hot-side temperature of the module at 473 K and ΔT of 200 K in the air with a load resistance of 0.1–0.75 kΩ, the module generated up to an output voltage (V_{out}) of 0.8 V, output current (I_{out}) out of 2.46 mA, maximum output power (P_{out}) of 1.98 mW and maximum conversion efficiency (η) of 0.15% were reported by Seetawan et al. (2014). The TE power generation was composed of small *n*-CMO and *p*-CCO of 31 couples/ in² and used a thin copper plate and

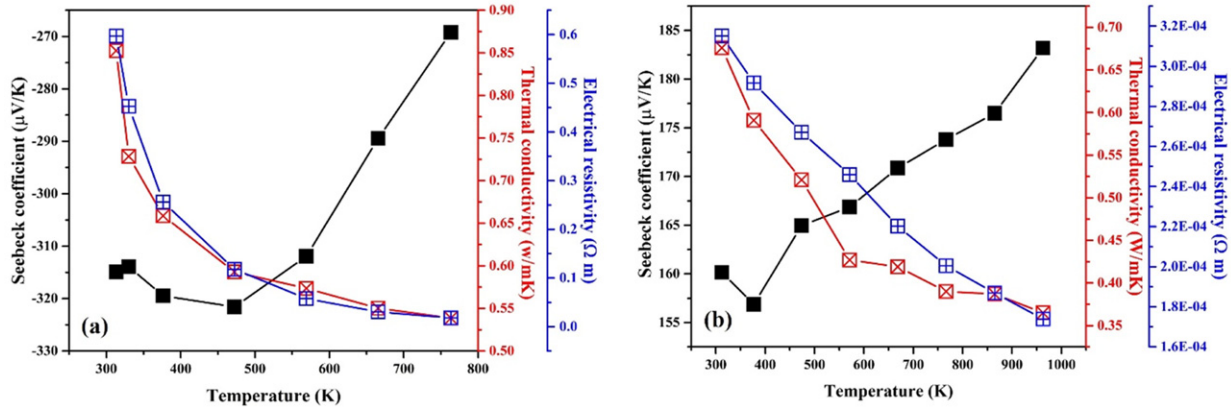


Fig. 4 The temperature dependence of the Seebeck coefficient and thermal conductivity of (a) the *p*-CCO and (b) *n*-CMO.

silver paint as electrodes, as reported by Phaga *et al.*, (2012). It was found that the mean voltage, current, and power were ~ 121.70 mV, ~ 0.012 mA, and ~ 1.47 μ W.

However, no pair of TE oxide materials can maintain a high TE performance over the entire service temperature range. To increase the overall performance of TE devices, combining different TE devices with successively distributed optimum working temperatures is a promising approach. Therefore, new heat exchangers for energy recovery are designed with different internal geometries or shapes to make the flow less disturbed. Optimizing heat exchangers is necessary to ensure that the maximum value of the transferred heat causes the minimum pressure to drop and that the system causes no more energy losses than necessary. Segmentation is an approach that has been suggested for TE modules. In a segmented leg, each *p*- and *n*-leg is constructed from at least two different *p*- and *n*-materials, respectively; that is, the materials in the leg are joined together electrically and thermally in series. In this structure, each TE device's *p*- and *n*-legs can be made from either a single material or segmentation (Pham *et al.*, 2019). However, the segmented element usually has an interface between sections. These interfaces can cause significant heat and electrical losses and lower the overall module efficiency.

No detailed reports on horizontal bulk oxide TE cells are available. Instead, we report a new innovative high-temperature TE cell comprising layered cobaltite $\text{Ca}_3\text{Co}_4\text{O}_9$ and perovskite CaMnO_3 , as shown in Fig. 5. This new design concept can thus integrate cell design (combining a small group of TE couples and removing external gaps) with the oxide TE material. In the *I*-*V* testing circuit, measurements are routine because standard digital multimeters can measure the magnitudes of the voltage (V) and current (A). The generated voltage and current are scanned at different points in less than 100 ms to obtain the *I*-*V* curves or operate the TEG under a dynamic load. The bulk TE cell improved the maximum output power for this type at $\Delta T = 473$ K.

p-CCO/*n*-CMO bulk power generation

The power generation of a module is unexpected under realistic working conditions, and many factors affect the output power of the cell, such as heat losses, contact resistances, and heat transfer. Different circuits were prepared, tested, and compared to demonstrate the influence of a bulk TE cell's horizontal shape. To understand the sources that influence the obtained experimental results, the relationship between the open-circuit voltage V_{OC} and the TEs forming the module can be expressed as (Rowe, 2018)

$$V_{OC} = n \int_{T_c}^{T_h} \{S_p(T) - S_n(T)\} dT \quad (12)$$

where T_h and T_c are the hot and the cold side temperatures, n is the number of *p*-*n* couples, S_p and S_n are the Seebeck coefficients of *p*-*n* legs, respectively.

One should note that the thermocouples used to measure the temperature were placed on the surface of Ag electrodes, and their thermal contact resistance was assumed to be small. Therefore, the V_{OC} measured values reflect the actual temperature span across the TE legs.

As for the horizontal shape TE device, the formula can be rewritten as:

$$V_{OC} = n \int_{T_m}^{T_h} \{S_{CCO}(T) dT - S_{CMO}(T)\} dT \quad (13)$$

where T_m denotes the temperature at the connection junction to the cold side. They T_m can be determined by the continuity of the heat flux at the junction, which yields (Apertet *et al.*, 2015, 2014)

$$\kappa_{CCO}(T_h - T_m) + S_{CCO}T_m = \kappa_{CMO}(T_m - T_c) + S_{CMO}T_m \quad (14)$$

In the case of the open circuit voltage, they T_m can be obtained by:

$$T_m = \frac{\kappa_{CCO}T_h + \kappa_{CMO}T_c}{\kappa_{CCO} + \kappa_{CMO}} \quad (15)$$

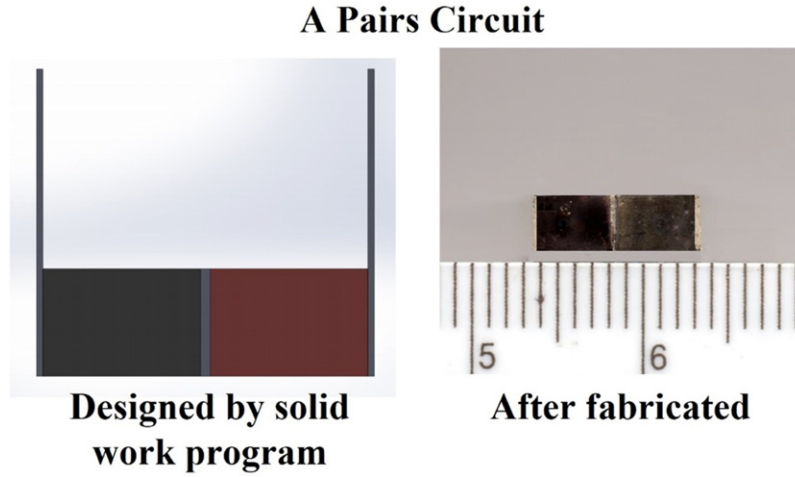


Fig. 5 Model design of p-n bulk TE cell configuration and after fabricated of the horizontal design.

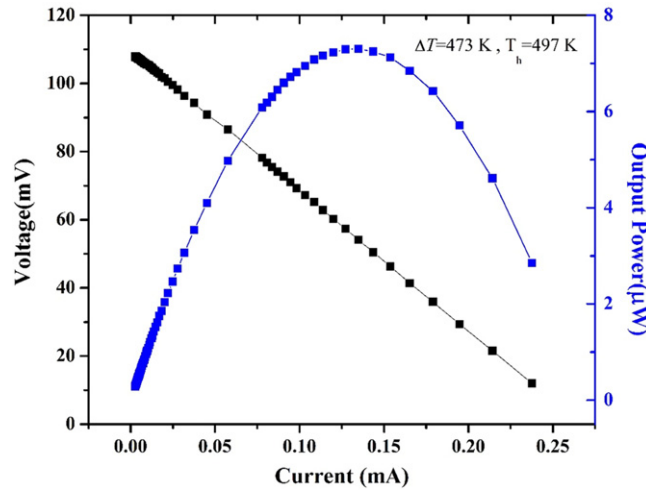


Fig. 6 The V - I and P - I curves of horizontal shape of bulk TE cell as a function of temperature difference at $T_h = 497$ K.

The magnitude of the output current (I) is proportional to the sum of the internal resistances of the device (R_{int}) and the external resistive load (R_{load}), and is given by

$$I = \frac{V_{OC}}{R_{int} + R_{load}} \quad (16)$$

where $R_{int} = R_{load} + R_C$ is the sum of the resistances of the p-n legs without metal electrodes (R_{legs}). Furthermore, the total contact resistance R_C includes the contact resistances at the joining part of the multilayer leg, hot-side junction, and cold-side junction. The power output of the module as a function of V_{OC} the total resistance is given by:

$$P = I^2 R_{load} = V_{OC}^2 \left[\frac{R_{load}}{(R_{int} + R_{load})^2} \right] \quad (17)$$

It is clear from Eqs. (11), (16), and (17) the power output of the module depends on the Seebeck coefficient, internal resistance, and external load resistance. It P_{max} occurs when the external load resistance is equal to the internal resistance. Therefore, to generate a TE cell with maximum power output, the load resistance must be continuously adjusted to match the resistance of the external device.

$$P_{max} = \frac{V_{oc}^2}{4R_{load}} \quad (18)$$

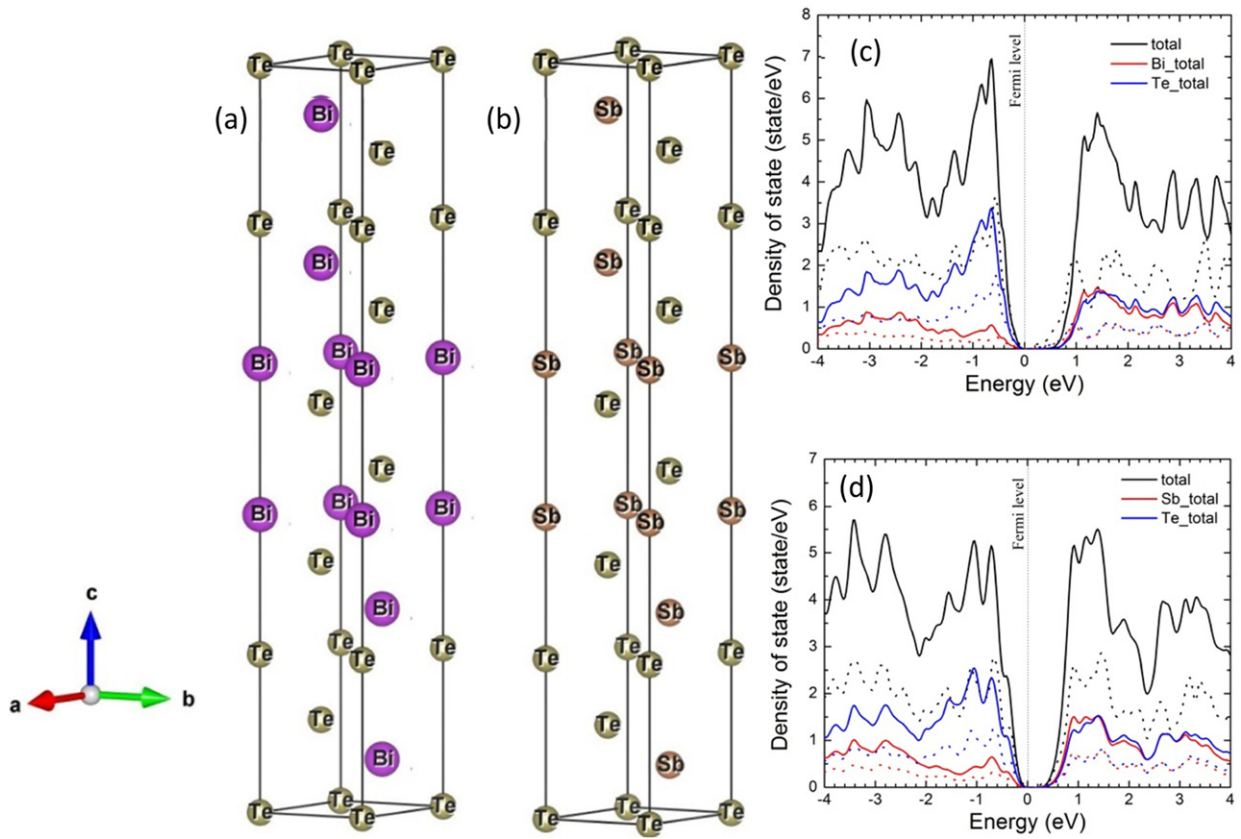


Fig. 7 Electronic structure of *p*-ST and *n*-BT calculated by VASP method (a) structural of *n*-BT, (b) structural of *p*-ST, (c) density of state of *n*-BT and (d) density of state of *p*-ST.

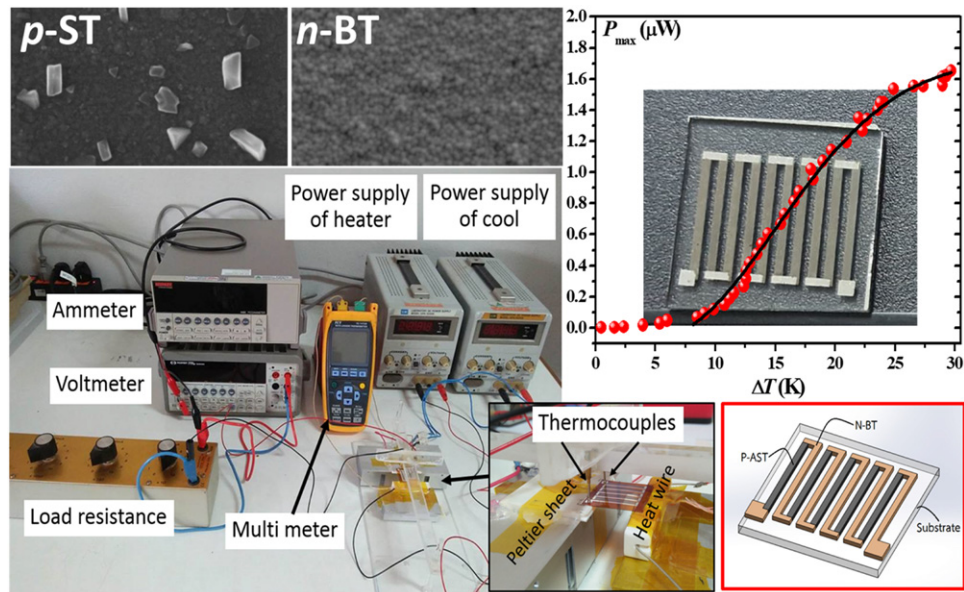


Fig. 8 Device fabrication and measurements.

This resistance can vary significantly with temperature because of the temperature dependence of the resistivity of the TE itself, as well as the temperature dependence of the total contact resistance. It was evident that the smaller the external resistance, the higher the maximum output power.

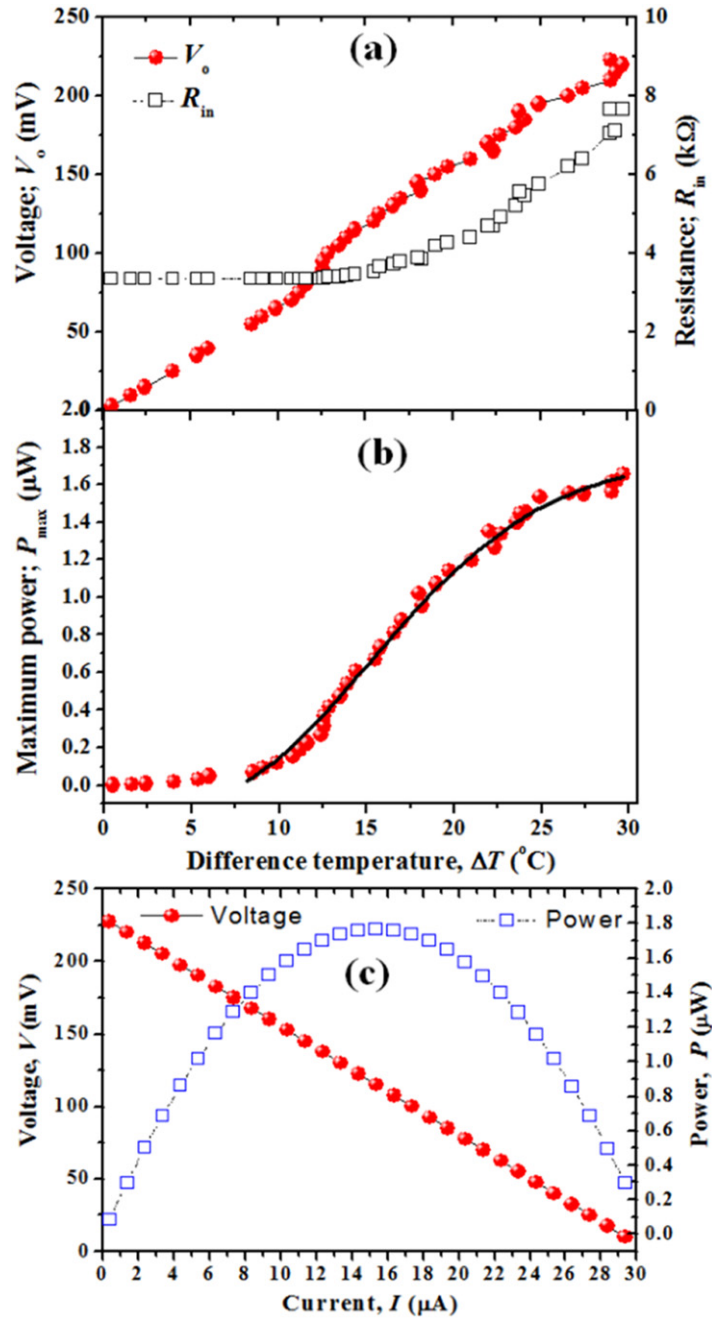


Fig. 9 Experimental results of (a) internal resistance and open circuit voltage and (b) maximum power versus difference temperature and (c) output voltage, power and current.

Fig. 6 shows the power generation characteristics of the modules under various applied temperature gradients. As expected, the voltage current $V(I)$ and output power current $P(I)$ show the same tendency to increase as the temperature increases. At the highest applied temperature difference ($T_h/T_c = 497\text{ K}/\sim 297\text{ K}$) $\Delta T \approx 473\text{ K}$, the V_{OC} TE device measured was 82.14 mV, and the voltage decreased linearly with increasing current. The measured maximum output power reached a value of 7.30 μ W at a current of 0.0026 mA and a voltage of 107.98 mV. The TE power generation was composed of small n -CMO and p -CCO of 31 couples/ in^2 and used a thin copper plate and silver paint as electrodes, as reported by Phaga *et al.* (2012). It was found that the mean voltage is ~ 121.70 mV, the current is ~ 0.012 mA, power is ~ 1.47 μ W. In comparison, Matsubara *et al.* (2001) reported the fabrication of an all-oxide TE power generator using the Gd-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ p -type legs and La-doped CaMnO_3 n -type legs. They were demonstrated with the eight p-n couples, the device generated output power of 63.5 mW under the thermal condition of hot side temperature $T_h = 1046\text{ K}$ and a temperature difference $\Delta T = 663\text{ K}$. From the above when compared the results from this work with literature reviews, the reason for this high electrical power is believed to be a result of the modified contact of the electrode

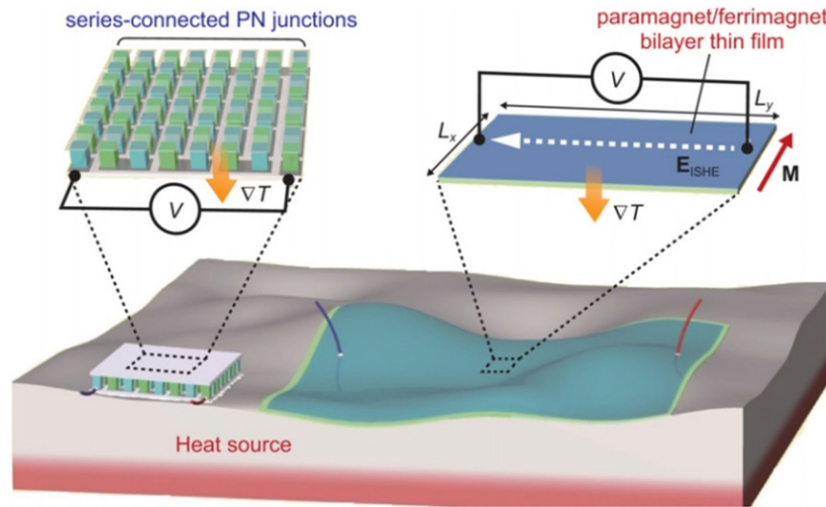


Fig. 10 Bulk TE and thin film STE devices on a heat source (body heat).

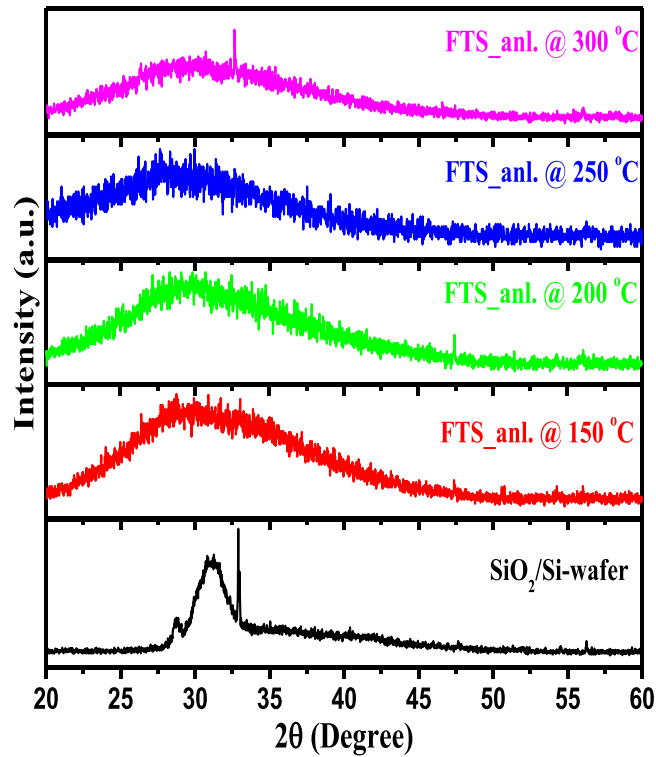


Fig. 11 XRD pattern of Fe-Ti-Sb thin films as temperature annealing function.

(brazing soldering process), the optimized material properties (hot-pressed process and nanoparticle effect), and we can reduce thermal losses because of good packing of thermal insulation with the design of the horizontal shape).

Thin Film TE Materials

$p\text{-Sb}_2\text{Te}_3/n\text{-Bi}_2\text{Te}_3$ Thin Film Materials

Based on enhancement of TE properties started first principal calculation within density functional theory (DFT) of electronic structure into a thin film and device fabrication. The electronic structure of $p\text{-ST}$ and $n\text{-BT}$ TE materials was calculated by Vienna

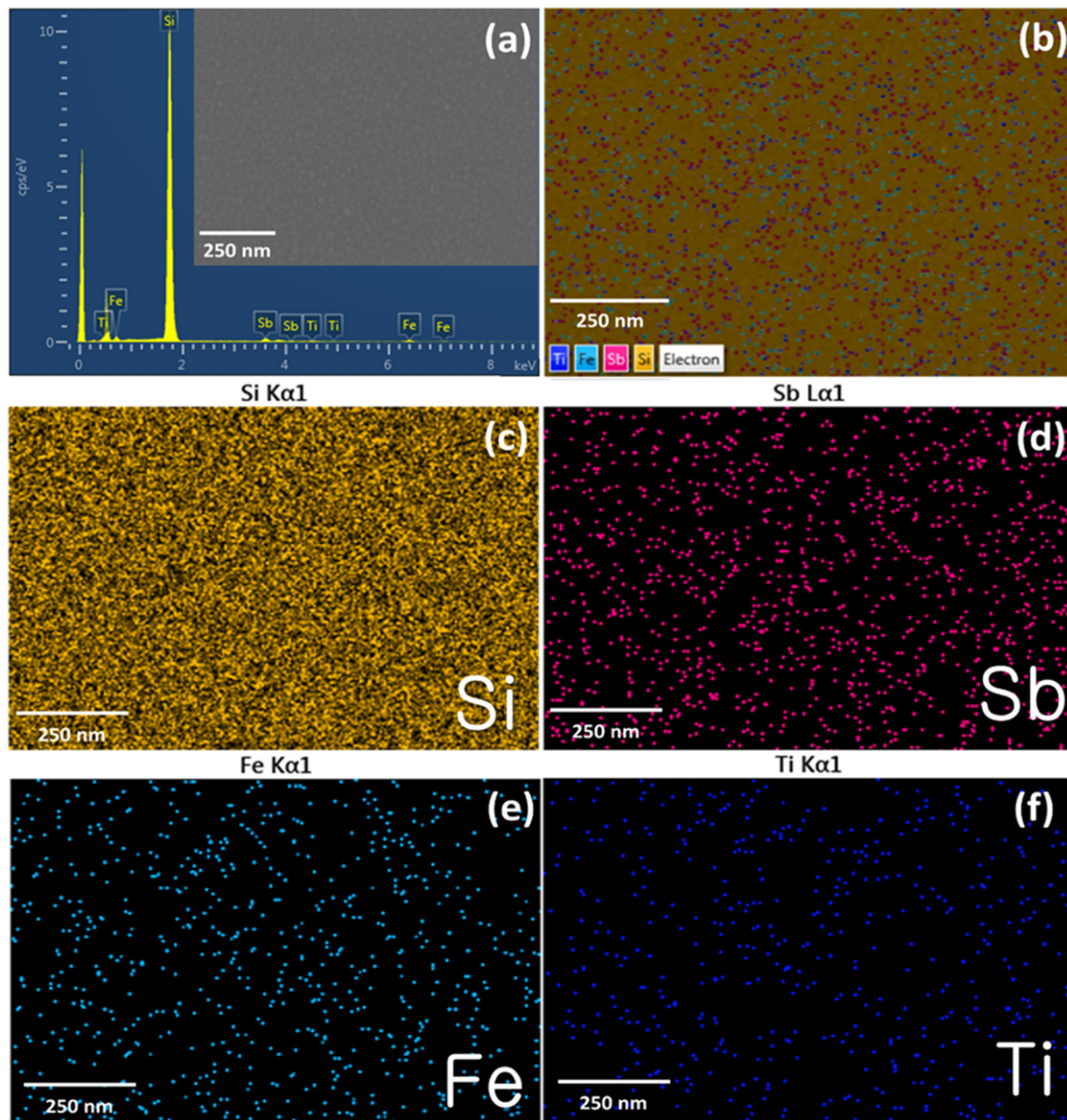


Fig. 12 EDX and mapping of atomic composition.

Ab-initio Simulation Package (VASP) method within exchange-correlation and generalized gradient approximation (GGA), as shown in Fig. 7.

p-Sb₂Te₃/n-Bi₂Te₃ Thin Film TE Device

A thin film TE generator has open circuit voltage, internal resistance, and maximum power generated in the range of temperature difference as obtained from the measurement results. A thin film TE generator of *p*-type (Silver-Antimony-Telluride, Ag-Sb-Te; AST) (Prainetr *et al.*, 2020a,b; Thaowonkaew *et al.*, 2021) and *n*-type (Bismuth-Telluride, Bi-Te; BT) (Vora-ud *et al.*, 2020) was fabricated by DC-magnetron sputtering method and used Ag thin film for the electrode. AST and BT thin films were deposited on glass substrates by DC magnetron from Sb: Te; 1:1 target of 99.99% purity (ULVAC Technologies, Inc.) and Bi: Te; 1:1 target of 99.99% purity (Mercantile hi-tech co. ltd.) for 3.0 in. of diameter and 0.25 in. of thickness.

p-Sb₂Te₃/n-Bi₂Te₃ Thin Film Power Generation

The TE properties of *p*-type and *n*-type materials were enhanced to fabrication of 5 pairs of thin-film elements, followed by the best condition of each material as shown in Fig. 8. The *p*-AST thin films were optimized through thermal annealing process due to the amorphous phase of as-deposited. In contrast, the *n*-BT as-deposited thin film showed crystalline. It was found that a thin film TE

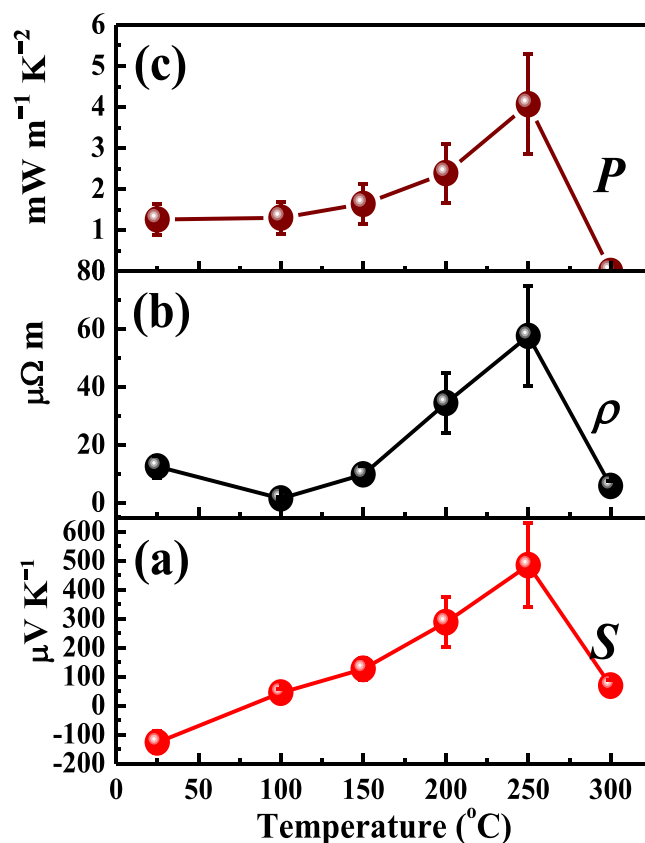


Fig. 13 TE properties of Fe-Ti-Sb thin films as temperature function.

generator had open circuit voltage, internal resistance, and a maximum power of approximately 223 mV, 7.67 kΩ, and 1.6 μW at a differential temperature of 30 K, respectively, as shown in Fig. 9.

Fe-Ti-Sb Spintronics Thin Film TE Device

A new approach for thin film TE based on spintronics TE, spintronics is a new electronic technology within the spin degree of free electrons (Wolf *et al.*, 2001). In this field, a spin counterpart of the Seebeck effect, so-called spintronic TE (STE), was discovered in 2008 (Uchida *et al.*, 2008) and developed into TE thin films (Uchida *et al.*, 2014) useful for wearable TE devices. Intelligent electronic devices promoted a new generation of small and genius electronic devices and facilities for everything in our life. Because it is possible to generate electricity with thin film TE devices using body heat. Also, they have promoted clean and green alternative energy for micro-power generators and sensors. The thin film STE, with a highly efficient process on a non-magnetic substrate due to the spin-current-driven TE conversion, is successfully demonstrated under a temperature gradient. The spintronic TE prototype of Fe-Ti-Sb thin films will be fabricated and applied to innovative wearable electronics from body heat, as shown in Fig. 10.

Based on this concept, we have prepared Fe-Ti-Sb thin films by the DC magnetron sputtering method onto SiO₂ 0.1 μm/Si-wafer substrates. The as-deposited thin films were annealed at 150–300°C within the rapid thermal annealing method under a vacuum atmosphere each for 1 min. The thin films were investigated on the microstructure, morphology, composition, and TE properties. The microstructure, morphology, and composition of the thin films were carried by X-ray diffractometer (XRD), field-emission scanning electron microscope (FE-SEM), and X-ray dispersive spectroscopy (EDX), respectively. Seebeck coefficient (S) and electrical resistivity (ρ) value of thin films were measured by the ZEM-3 method from room temperature to 300°C. Fig. 11 shows the XRD result to be indicated the metallic-glass structure of the thin film. The SEM and EDX results of the thin film confirmed the metallic-glass surface and indicated the Fe₅TiSb₄ composition, as shown in Fig. 12. TE properties of the thin film could be transferred from n-type to p-type depending on the temperature, as shown in Fig. 13. The highest power factor was 1.26 mW m⁻¹ K⁻² at room temperature and 1.26 mW m⁻¹ K⁻² at 250°C for n-type and p-type, respectively.

Future Directions

The electrical power of bulk and thin film TE devices will be developed 2D materials for high performance and many applications.

Conclusions

TE nanogenerators, microgenerators, and more excellent and small refrigerators are solid-state energy harvesting sources. We prepared nano-powder by planetary ball mill and synthesized the bulk TE by hot pressing method and the film TE synthesized by multi magnetron sputtering method. We applied the bulk & film TE devices in harvesting energy to nano and microsensors, small charging systems, and personal cooling systems depending on low temperature, medium temperature, and high-temperature heat side or different temperatures. We have a prototype of personal temperature control, helmet temperature control, heat pump, and the future of air conditioners.

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From 3.8% to over 23.8% Power Conversion Efficiency: Commercial Perovskite Solar Cells, Significant Manufacturing Techniques, and Future Prospects

Arkashis Paul, Baidurya Sarkar, Swastik Paul, and Sk Abdul Moyez, Department of Chemical Engineering, University of Calcutta, Kolkata, India

Hyun Suk Jung, School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Korea

Subhasis Roy, Department of Chemical Engineering, University of Calcutta, Kolkata, India

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Abstract

The advanced perovskite solar cells (PSCs) have attracted due attention of the world research society for their high-efficiency achievement quickly. Also, the reduction of the efficiency of PSCs with an increase in the surface area being of much lesser extent makes PSCs more suitable for large-scale power generation and puts them at the top as the best alternative source of energy for the future. But the upscaling of perovskite solar cells, high power conversion efficiency, and optimum stability are also challenging factors towards the commercialization of this technology. Proper fabrication techniques for PSCs could be an essential factor for industrializing this advanced photovoltaic (PV) technology because the manufacturing technique may mitigate the instability tendency and increase the efficiency of the commercialized PSCs as per industrial needs. Generally, different solution processing methods and vapor techniques have been employed for upscaling the PSCs. Hence, this review article will discuss the effective manufacturing techniques and prospects of this emerging perovskite solar cell by summarizing the recent progress of large-area-based PSCs and various manufacturing techniques in detail.

Key Points

- Manufacturing techniques for the fabrication of Perovskite solar cells
- Solution-based and vapor technology
- Large-area-based perovskite solar cells
- Film quality with high purity and high power-conversion efficiency

Introduction

The increasing global energy demand could be reached 16 terawatts within 2030, as predicted by the scientists, (Castro-Hermosa *et al.*, 2016) which may be difficult to mitigate by the traditional fossil fuels due to their limited resources and harmful impact on the environment. Scientists have predicted that oil, gas, and coal energy may end up by 2052, 2060, and 2090 respectively; hence the use of renewable energy from wind, solar, and biogas resources is gaining popularity (Olave-Rojas *et al.*, 2017). But among the varieties of all renewable energy resources, solar energy is the most viable and popular energy source due to its constant availability with minimum environmental and ecological hazards associated with its production. The already established silicon solar cells have the highest market share in the solar energy sector. Still, it took a long time to develop silicon solar cells as conventional technology in the market field (Zhou *et al.*, 2018; Moyez *et al.*, 2020). Besides silicon solar cells, other modern PV technologies are also up-and-coming, but they are limited by efficiency, processing technique, or their impact on the environment, (Maitra *et al.*, 2021; Mathew *et al.*, 2014; Roy *et al.*, 2015; Moyez and Roy, 2017). But in 2009, Japanese scientists Miyasaka *et al.* first developed promising thin film-based perovskite solar cells (PSCs) using organic-inorganic hybrid halide material (methylamine lead iodide) $\text{CH}_3\text{NH}_3\text{PbI}_3$, with a power conversion efficiency (PCE) of 3.8% (Kojima *et al.*, 2009). The popularity of PSCs has become skyrocketed over the last few years due to their high efficiency, cost-effectiveness, simplicity in manufacturing, and photovoltaics properties like high charge carrier mobility, large dielectric constant, long carrier (electron and hole) lifetime, and effective transmission of electron and hole, etc. Besides many advantages, the crucial challenge for PSCs is their degradation or instability tendency; hence, after developing PSCs, researchers have investigated it in different aspects to increase stability simultaneously with efficiency. In 2012, Kim *et al.* increased the efficiency of perovskite solar cells to 9.7% (Kim *et al.*, 2012) by utilizing the all-solid-state technique, while the certified efficiency for PSCs reached 22.1% within 2016 (Yang *et al.*, 2015). The efficiency of PSCs increased further to 23.8% later on, in 2020, by Subbiah *et al.* (2020). for a 2-terminal -monolithic tandem solar cells with PCE of 23.8% for the device with an active area of 1 cm^2 . Researchers have focused on increasing the efficiency of PSCs and developed different techniques or employed wide varieties of manufacturing techniques to encounter the instability issue with efficiency enhancement simultaneously. Moyez *et al.* fabricated the most promising $\text{CH}_3\text{NH}_3\text{PbI}_3$ based PSC by developing a new dual step thermal engineering technique. This type of PSCs is essential to industrializing this revolutionary development (Moyez and Roy, 2018). The increasing efficiency of PSCs with time and its present challenges are shown in Fig. 1.

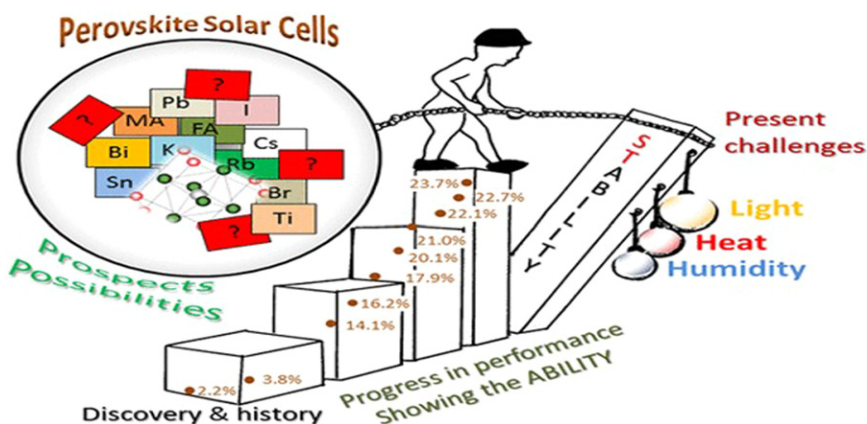


Fig. 1 Increasing efficiency of perovskite solar cells with time and its present challenges. Reproduced with permission Jena, A.K., Kulkarni, A., Miyasaka, T., 2019. Halide perovskite photovoltaics: Background, status, and future prospects. *Chemical Reviews* 119 (5), 3036–3103. Available at: <https://doi.org/10.1021/acs.chemrev.8b00539>. Copyright 2019, American Chemical Society.

The researchers have developed/employed different techniques for developing PSCs, which could play a crucial role in stabilizing PSCs. Hence, this review will discuss other fabrication techniques to develop PSCs. The role of a different fabrication technique for PSCs impacts its stability and efficiency. We also focus on the cost-effectiveness of the other methods used for PSCs research in this review. This review paper has been divided into different chapters like the structure of a mesoporous PSC, working of a PSC, an overview of manufacturing techniques, solution-processed PSC, roll to roll processed PSC, vapor technology processed PSC, and finally concludes the whole theme.

Structure of a Mesoporous Perovskite Solar Cell

A typical mesoporous PSC generally consists of the layer of FTO-glass substrate, compact electron transport material (ETM)/electron transport layer (ETL), a mesoporous oxide layer, light-absorbing perovskite material, hole transporting materials (HTM), and metal electrode. The different layers of mesoporous PSCs have been represented in Fig. 2(i). In this photovoltaic device structure, TiO_2 is one of the significant materials used to transport electrons from perovskite material towards FTO and electrode. The TiO_2 layer also acts as a blocking layer for holes and resists recombination of the exciton in the FTO substrate by preventing holes from entering it. In this way, the TiO_2 layer helps to improve the device performance of the PSCs. So, in perovskite device structure, TiO_2 is mainly used as ETL/ETM. The hole transport layer extracts holes from the perovskite layer and transports them to the metal electrode. The most widely used HTM in PSCs is Spiro-OMeTAD, so far. Fig. 2(ii) depicts the short circuit current density vs. voltage characteristics of PSCs.

Working of a Perovskite Solar Cell

The perovskite semiconducting material's layer produces excitons or electron-hole pairs during exposure to sunlight by absorbing the photons. There are two possibilities: either electrons will form free carriers (free electrons and holes) or recombine. But due to the lower exciton binding energy, higher carrier mobility, longer diffusion distance, and long carrier lifetime, the excitons generally form free carriers. And, these free electrons and holes are transported to the electrode through ETL and HTM, respectively, and generate electricity for the well connected external-circuit device.

Overview of Manufacturing Techniques

The manufacturing techniques of PSCs using conventional processes can be sub-categorized, as shown in Fig. 3.

Solution-Processed Perovskite Solar Cell

The solution processing technique has become the most popular method in laboratory-scale research to fabricate a perovskite PV device. Fabrication of perovskite layer by solution processing method is a promising manufacturing technology because of its low production cost and simplicity. In case of ABX_3 ($\text{A} = \text{CH}_3\text{NH}_3/\text{Cs}/\text{NH}_2\text{CH} = \text{NH}_2^+$, $\text{B} = \text{Pb}/\text{Sn}/\text{Ge}$, $\text{X} = \text{I}/\text{Br}/\text{Cl}$) perovskite formation, generally, the desired stoichiometric ratio of BX_2 and AX dissolve in a solvent to prepare the precursor solution.

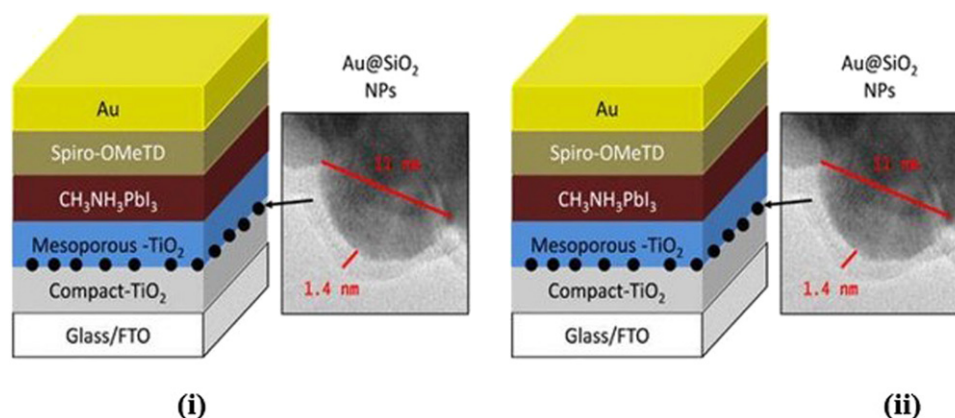


Fig. 2 (i) Different layers of perovskite solar cell and SEM analysis of perovskite layer. (ii) Short Circuit Current Density vs Voltage characteristics. Reproduced with permission Aeineh, N., Barea, E.M., Behjat, A., Sharifi, N., Mora-Seró, I., 2017. Inorganic surface engineering to enhance perovskite solar cell efficiency. ACS Applied Materials & Interfaces 9 (15), 13181–13187. Available at: <https://doi.org/10.1021/acsami.7b01306>. Copyright 2017, American Chemical Society.

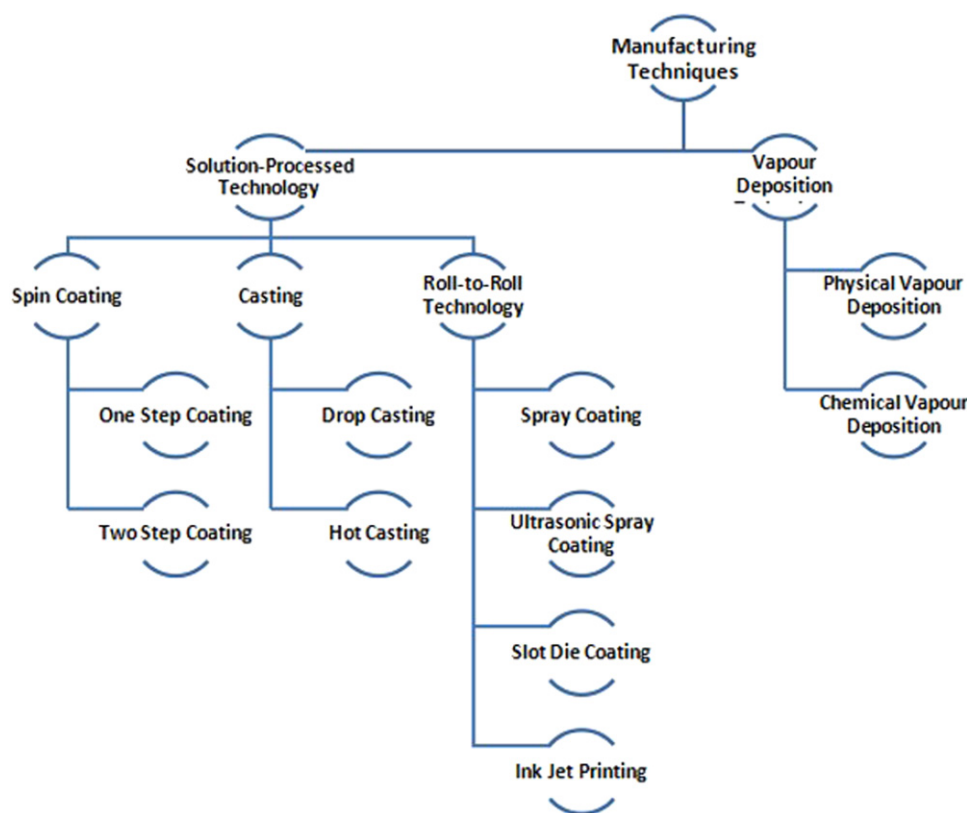


Fig. 3 Classification of perovskite solar cell manufacturing techniques.

The precursor solution is then transferred to the substrate/PV device by various techniques and dried at a suitable temperature and pressure to evaporate the solvent. Then the desired light-absorbing perovskite layer or materials is obtained, as illustrated in Fig. 4. The scheme illustrates the improved morphology of the perovskite thin film with solution processing-based technique. In 2015, Chen *et al.* successfully prepared large area-based (1 cm²) PSCs with a PCE of 15.0%. But the PCE for a 1 cm² area-based device reached 19.7%, which is close to the efficiency of 22.1% achieved for the PSCs device with a 0.046 cm² area (Yang *et al.*, 2017). The highest recorded efficiency by this technique is about 23.8% for a 1 cm² device. The biggest challenge of this method is to control the desired crystal formation with uniform, pin-hole-free smooth films over a large area with the right drying time. Another big challenge is making the perovskite layer's fabrication more tolerant to the surrounding environment for large-scale production. The solution-processing-based deposition is accomplished using different technologies such as spin coating, casting, spray coating,

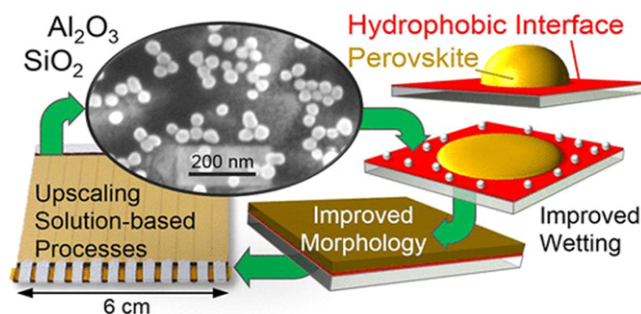


Fig. 4 Schematic illustration of improvement of the morphology of the perovskite layer by solution processing. Reproduced with permission Schultes, M., Giesbrecht, N., Küffner, J., *et al.*, 2019. Universal nanoparticle wetting agent for upscaling perovskite solar cells. *ACS Applied Materials & Interfaces* 11 (13), 12948–12957. Available at: <https://doi.org/10.1021/acsami.8b22206>. Copyright 2019, American Chemical Society.

ultrasonic spray coating, slot die coating, inkjet printing, etc. Spin coating and casting are the simple and low-cost methods than others; nevertheless, they can not produce uniform film thickness for large-area PSCs where roll-to-roll solution-processed manufacturing technique of PSC, including spray coating, ultrasonic spray coating, slot-die coating, inkjet printing gives uniform film thickness and better PCE. So, the roll-to-roll technique is more efficient for large-scale PSC production.

Spin Coating Technique

Spin coating is the popular, simplest, and economical solution process fabrication technique employed to fabricate perovskite thin films. The spin coating needs a small amount of precursor solution to form the thin film. In this process, mainly the precursor solution keeps at the center of the substrate, and the substrate rotates at a very high speed by spin coater. The solution material is spread radially from the center to the end by centrifugal force (Schultes *et al.*, 2019). In some cases, the solvent used to prepare the precursor solution is volatile. So, it may evaporate entirely simultaneously during the high-speed rotation of the substrate. But in the case of PSCs, the solvent may remain within the thin film, so the thin film prepared after spin coating needs to be dried at the desired temperature. After that, the dried perovskite film is obtained. The perovskite precursor solution has been spin-coated over a mildly hot substrate followed by rapid annealing after spin coating forms better perovskite thin film in the dual-step thermal engineering technique. The perovskite thin-film or fabricated PSCs by spin-coating approach is shown in Fig. 5. Generally, (1) one-step spin coating (2) two-step spin coating method is used in case of PSCs formation, which has been discussed below.

One step spin coating

The one-step spin coating technique was first employed by Miyasaka *et al.*, who first developed hybrid halide PSCs. During one-step spin coating of methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) upon the substrate, at first, the equimolar amount of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 dissolves in a proper solvent like N, N-dimethylformamide (DMF)/dimethyl sulfoxide (DMSO). After that, the substrate is rotated, or spin coating is applied using a spin coater, and proper heat treatment or thermal energy is required for that spin-coated film to evaporate the solvent. This methodology has achieved 22.1% efficiency for a device with an active area of 0.046 cm^2 , and it has been the highest PCE for one-step spin-coating till now. Pan *et al.* fabricated hydrochloride-assisted highly smooth PSCs by one-step spin coating method at room temperature, which gained an efficiency of 15.7% for the 0.86 cm^2 active area device. Chiang *et al.* employed the one-step spin coating technique to prepare large-area PSCs with an active area of 25.2 cm^2 which gained an efficiency of 14.3%. Qiu *et al.* also used this technique to achieve 13.6% efficiency for a 4 cm^2 device successfully without pinhole formation (Qiu *et al.*, 2016). Di Carlo *et al.* (2014) prepared large-area PSCs (aperture area: 2.52 cm^2) by this technology with an efficiency of 7.6%.

Two-step spin coating

The synthesis of PSCs by spin coating is bound to the one-step spin coating process. The two-step spin coating technique also addresses some crucial challenges in PSCs like smooth film formations, efficiency enhancement, and counter instability. In this process, perovskite thin film is prepared by the two-step spin-coating, unlike single-step spin coating, which was first applied in the PSCs field by Liang *et al.* (1998). In this method, in the case of $\text{CH}_3\text{NH}_3\text{PbI}_3$ formation, the different precursor solutions of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ is prepared using methanol and 2-propanol solution. First, the PbI_2 precursor solution is spin-coated on the top of the PV substrate holder followed by submerged in the $\text{CH}_3\text{NH}_3\text{I}$ precursor solution, prepared using 2-propanol, for some time. Then the solution is dried for the volatilization of the solvent, and the $\text{CH}_3\text{NH}_3\text{I}$ reacts with PbI_2 , which forms the desired perovskite thin film. The two-step spin coating technique proved its efficacy as the Burschka *et al.* prepared PSCs with an efficiency of 15%. Though the efficiency achieved by this technique for a small area, PSCs is highly appraisable, this technique is limited to the large-area-based uniform perovskite film formation. Including that, the wastage of massive materials, formation of pinholes, and slow processing make this technique a not viable solution for the commercialization of large area-based PSCs.

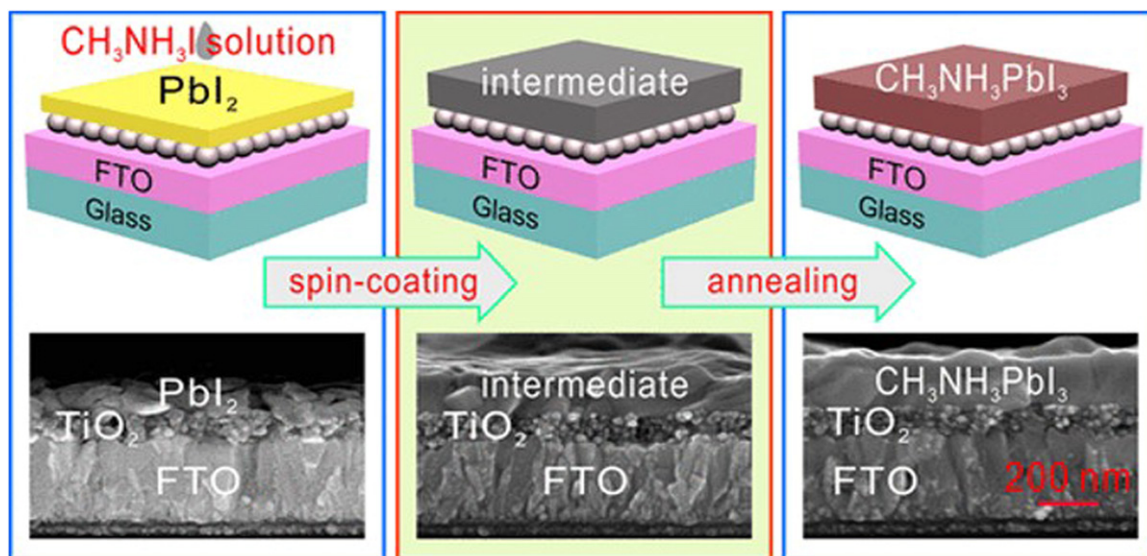


Fig. 5 Schematic diagram of spin-coated perovskite solar cell. (Reproduced with permission Chen, J., Wan, Z., Liu, J., *et al.*, 2018a. Growth of compact $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films governed by the crystallization in PbI_2 matrix for efficient planar perovskite solar cells. *ACS Applied Materials & Interfaces* 10 (10), 8649–8658. Available at: <https://doi.org/10.1021/acsami.7b18667>. Copyright 2018, American Chemical Society).

Casting

Casting is an attractive and cost-effective solution processing method for preparing PSCs. The perovskite precursor solutions are transferred to the targeted substrate and heated to remove the solvent. Casting is quite similar to spin coating, while no spinning is required in this process. The film thickness could be controlled to some extent in the spin coating process, whereas controlling film thickness for casting is difficult because the thickness of the film for casting depends on many factors like volume of the dispersion and concentration and solid content in the perovskite precursor solutions. Besides, factors like the viscosity of perovskite solution, the surface tension of perovskite precursor solution and target substrate, and heating temperature significantly impact the desired film's quality. The casting process generally includes (1) drop-casting and (2) hot casting.

Drop Casting

In the drop-casting method, the precursor solution is drop-casted on a heated substrate and then spontaneously spreads to form a smooth, uniform layer upon drying. Mei *et al.* (2014) achieved a PCE of 12.8% for a small area-based printable mesoporous PSCs by adding 5-aminovaleric acid (5-AVA) into the γ -yrolactone solution containing PbI_2 and MAI. The addition of 5-AVA forms a new mixed-cation perovskite film $((5\text{-AVA})_x(\text{MA})_{1-x}\text{PbI}_3)$ which lowers the defect concentration and improves the pore filling in the mesoporous TiO_2 layer that led to developing a high performed device. Later, a large area-based (active area 7 m^2) printable PSCs were fabricated by Hu *et al.* (2017). PSCs containing drop-casted n-ylammonium-based quasi-2D perovskites achieved a PCE of 14.9% for PSCs manufactured under ambient conditions (Zuo *et al.*, 2018). So, it is suggested that the drop-cast method could be an effective route for upscaling high-efficiency solar cells. This method achieved the highest PCE of 16% for PSCs prepared with N_2 blow-dried iso-BA-based quasi-2D perovskite precursor solution (Zuo *et al.*, 2020).

Hot casting

The hot casting technique has recently been developed to deposit high-quality perovskite thin films. This technique has notable advantages, including rapid crystallization, quick film formation, large grain size, preferred crystalline orientation, and low defect states. The high temperature used in this process to substrate works as the necessary driving force for the phase change, which minimizes the crystallization process. Meanwhile, sufficient thermal energy also facilitates the diffusion of atoms in a liquid without forming an intermediate phase (Liao *et al.*, 2020). Nie *et al.* first introduced this method to create perovskite film, which further improved the film quality by optimizing the deposition parameters like substrate temperature, annealing temperature, and precursor composition (Faibut *et al.*, 2019). Nie *et al.* (2015) also reported the fabrication of a millimeter size grain of perovskite films for the first time with a PCE of 17.48% and negligible hysteresis. Liao *et al.* (2016) enhanced the device performance with controlled Cl^- incorporation using a hot-casting process and achieved a PCE of 18.2% for small areas (0.09 cm^2) PSCs and 15.4% PCE for a large area (1 cm^2) PSCs. Chen *et al.* (2018b) deposited an 850-nm-thick perovskite film with a PCE of 19.54%, while Tsai *et al.* (2016) achieved an efficiency of 12.52% without hysteresis based on $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ 2D perovskite. According to Hsiao *et al.*, the drop-casted PSCs with TEACI passivation could improve the efficiency from 15.44% to 18.89% compared to the PSCs without passivation shown in Fig. 6 and Fig. 7 (Hsiao *et al.*, 2019). The prominent advantage of the hot casting method is that no special equipment is required in this method, and the material wastage is more minor.

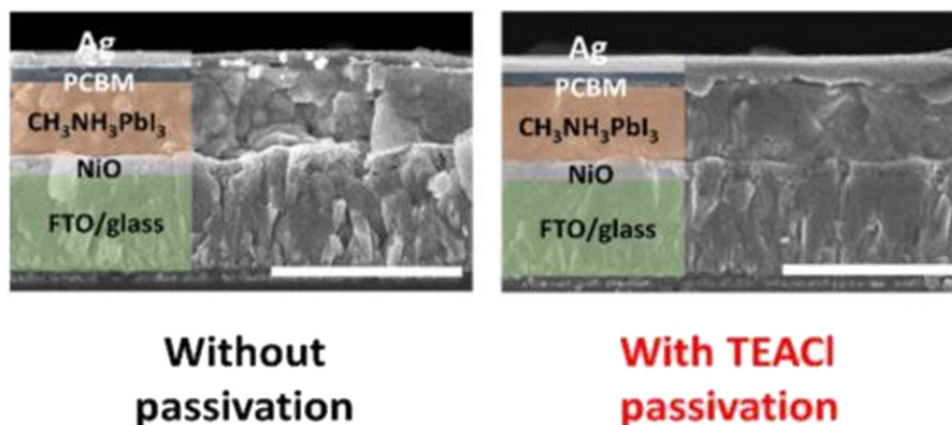


Fig. 6 Schematic diagram of hot-casted perovskite solar cell without passivation and with TEACl passivation. Reproduced with permission Hsiao, K.-C., Jao, M.-H., Li, B.-T., *et al.*, 2019. Enhancing efficiency and stability of hot casting p-i-n perovskite solar cell via dipolar ion passivation. *ACS Applied Energy Materials* 2 (7), 4821–4832. Available at: <https://doi.org/10.1021/acsaem.9b00486>. Copyright 2019, American Chemical Society.

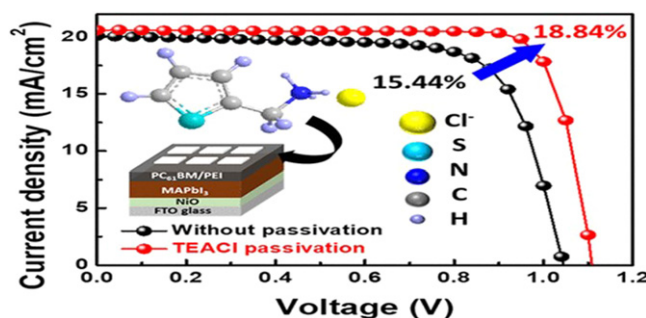


Fig. 7 Current density-Voltage characteristics and efficiency for hot-casted perovskite solar cell without passivation and with TEACl passivation. Reproduced with permission Hsiao, K.-C., Jao, M.-H., Li, B.-T., *et al.*, 2019. Enhancing efficiency and stability of hot casting p-i-n perovskite solar cell via dipolar ion passivation. *ACS Applied Energy Materials* 2 (7), 4821–4832. Available at: <https://doi.org/10.1021/acsaem.9b00486>. Copyright 2019, American Chemical Society.

However, this method has various shortcomings like difficulty in controlling the film thickness and non-uniform film formation on a large substrate. The large-area perovskite film can be fabricated by this technique but controlling the film thickness is an obvious drawback for large-scale production.

Roll to Roll Processed Perovskite Solar Cell

Roll to roll processing is one of the best solution processing techniques and holds excellent scope for large-scale and high-efficiency PSCs. The process creates functional films by integrating large-area manufacturing processes into a single manufacturing line, thus being highly efficient and cost-effective. It involves continuous processing of the flexible substrate as it is conveyed along a roller-based processing line. The entire processing line can be treated as a web, with the substrate getting loaded at one end, getting processed progressively as it moves through the web, and finally getting removed from the web at the other end (Schwartz, 2006). However, the properties of the substrate may change as it moves downstream, thus impacting the stability of the entire web. This process deposits various layers on a flexible substrate for PSCs to achieve high efficiency. Most of the solution-based deposition techniques are compatible with roll-to-roll processing for large-scale production. The best results have been obtained from the combination of slot-die processing and roll-to-roll processing, thus achieving solar cells with PCEs as high as 23.8% on 1 cm² area¹³. **Fig. 8(i)** illustrates the typical coupling of a roll to roll and slot-die coating techniques for producing high-efficiency PSCs for large areas by Lee *et al.* in 2019 (Lee *et al.*, 2019a). Current density-Voltage characteristics for the active area of 0.125 cm² and 16 cm² have been shown in **Fig. 8(ii)** and **(iii)**. This is due to the highly uniform films formed with these two coupled processes. Thus, roll to roll processing is highly efficient in depositing the various layers on PSCs. The most significant advantage of this kind of deposition is that very long wafers can be used, leading to the bulk production of solar cells, thus being a faster, highly scalable, and cost-effective technique.

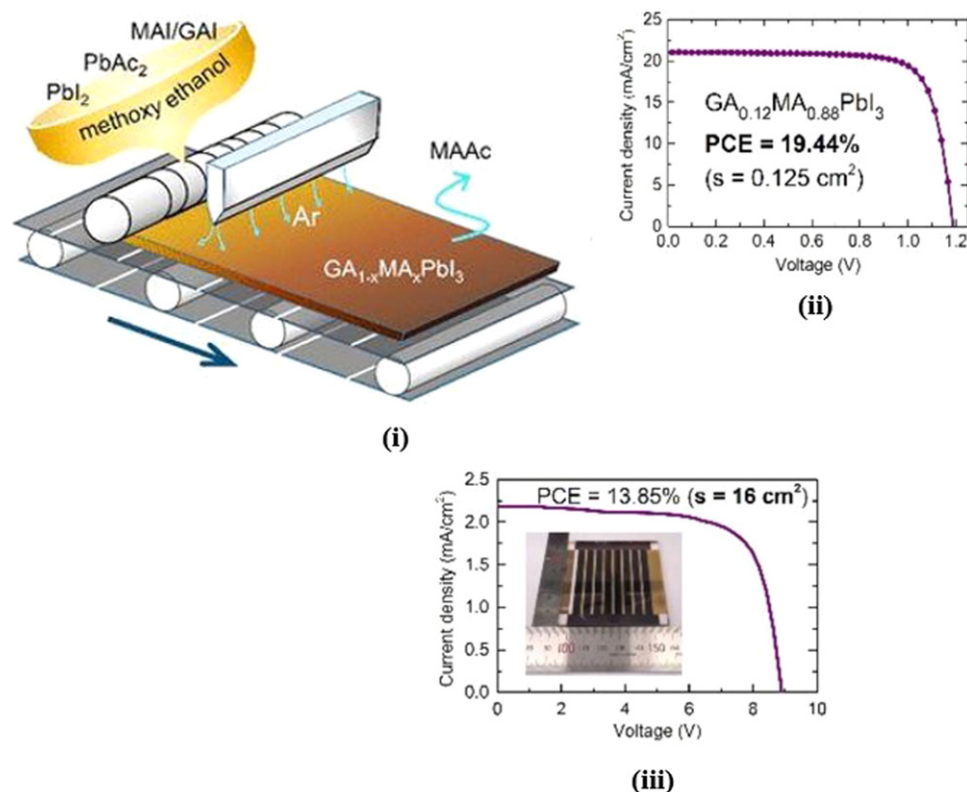


Fig. 8 (i) Schematic diagram of the roll to roll production process by coupling with slot die coating; (ii) Current density-Voltage characteristics for the active area of 0.125 cm^2 (iii) Current density-voltage characteristics for a large-area perovskite solar cell with 19% efficiency. ACS Energy Letters 4. Jeong, D.-N., Ahn, T.K., Park, N.-G., 2019b. Precursor engineering for a large-area perovskite solar cell with 19% efficiency. ACS Energy Letters 4. Available at: <https://doi.org/10.1021/acsenergylett.9b01735>. Copyright 2021, American Chemical Society.

Spray Coating

Spray coating is one of the most efficient, faster, and ease-scalable solutions processing methods for fabricating large-area-based perovskite thin films. The precursor solution sprays onto the substrate holder to form the film in this process. The quality of the fabricated film is controlled by the conditions of the nozzle flow rate, the droplet size of sprayed suspension, spray angle, and the temperature of the receiver substrate (Lee *et al.*, 2019b). This technique has many advantages over other spin-coating methods. The spray coating is highly scalable, while the spin coating is suitable for small-scale thin film deposition.

A typical spray coating system contains a pressure tank for precursor solution and an air-driven spray nozzle. The nozzle is used to spray the ultrafine droplets of the solution to the targeted substrate. The droplets spread over a surface undergo coalescence to form a uniform wet film which needs thermal energy to evaporate the solvent to form a solid thin film. This method exhibits high uniformity for large area-based thin film. But control of film thickness is difficult and crucial if the solution dries quickly because the droplets will not get sufficient time to merge to form a uniform layer over a large area (Bishop *et al.*, 2018a).

Conversely, a long drying time may also hamper the thin film leading to poor coverage. A complex parameter space must be optimized to create a high-quality film that includes surface temperature, solution flow rate, solvent choice, and spray-head height. The deposition technique of perovskite thin film using the spray-coating process is shown in Fig. 9(ii), and the corresponding current-density characteristics are shown in Fig. 9(ii).

A 25 cm^2 large, pinhole-free perovskite thin film has been prepared in this method (Habibi *et al.*, 2017). The automated spray coater may be able to control the roughness and film thickness by optimizing the temperature of the substrate and concentration of perovskite solution. The qualitative perovskite film and reproducibility are possible through this method. A promising 11% efficient PSCs have been achieved by this method by Barrows *et al.* (2014). Using a 3:1 blend of $\text{MAPbI}_{3-x}\text{Ac}_x$ to $\text{MAPbI}_{3-x}\text{Cl}_x$, Tait *et al.* demonstrated PCE of 15.7% for PSCs (Tait *et al.*, 2016). But the highest efficiency obtained for PSCs by this method is 17.8% (Bishop *et al.*, 2018b). One of the significant advantages of this technique is the rapid film deposition. Besides, various other advantages of this technique are low-cost processing and deposition capability for large scale both on flexible and glass-based substrates. Moreover, the spray-coated films exhibit higher thermal stability and better optoelectronic properties than spin-coated films due to better charge transfer capability and higher minority carrier lifetime (Bishop *et al.*, 2018b). This technique is compatible with the deposition of both planar and inverted PSC devices.

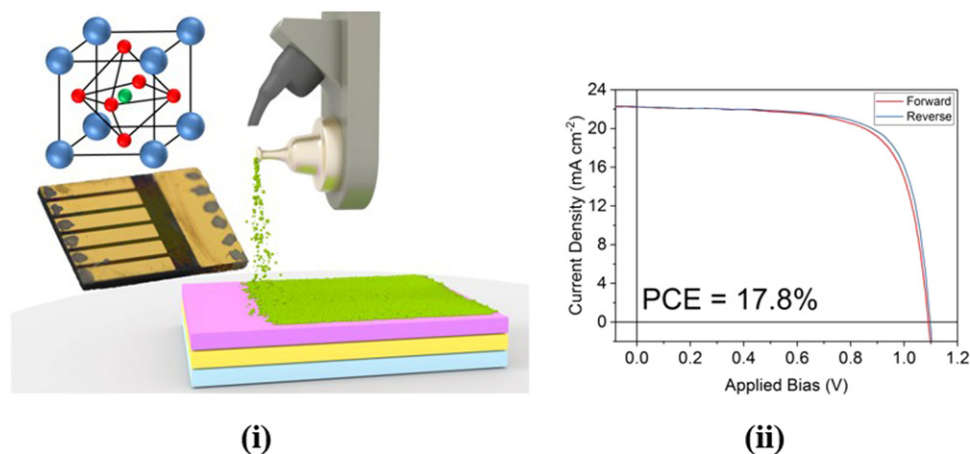


Fig. 9 (i) Schematic illustration of spray-coating perovskite film deposition technology. (ii) Current density-voltage characteristics for spray-coated perovskite solar cell. Reproduced with permission Bishop, J.E., Smith, J.A., Greenland, C., *et al.*, 2018b. High-efficiency spray-coated perovskite solar cells utilizing vacuum-assisted solution processing. *ACS Applied Materials & Interfaces* 10 (46), 39428–39434. Available at: <https://doi.org/10.1021/acsami.8b14859>. Copyright 2018, American Chemical Society.

Despite so many advantages, the highly homogeneous and fully covered layers are complicated to achieve by this spray coating technique because the random spraying of different size droplets leaves patches of varying sizes during drying. These advantages may lead to increases in the series resistance, affecting the device performance. So, the further modified ultrasonic spray coating technique is used to overcome this problem.

Ultrasonic Spray Coating

The ultrasonic spray coating technique is a further extension and modified spray coating technique. This technique has proper control over the deposition rate and is highly preferable for two-step deposition. The ultrasonic spraying technology was employed to deposit TiO₂ nanoparticles on polyvinylpyrrolidone (PVP) polymer substrate to fabricate PSCs by Bose *et al.* (2013).

Film formation mechanism

Zhou *et al.* (2017) described the ultrasonic spray coating deposition of TiO₂ nanoparticles using ethanol as a medium to prepare the precursor solutions. Ultrasonic waves generated the vibration caused the coating solution to spread over the atomized surface, and the solution was sprayed over the substrates to produce a compact TiO₂ film. They added titanium di-isopropoxide bis (acetylacetonate) to the TiO₂-ethanol solution at a mole ratio of 1 mol% to further improve the film quality. They suggested that the flow rate of TiO₂-ethanol solution, gas flow pressure, the distance between spray nozzle and substrate, and the moving speed of the nozzle influence the uniformity, roughness, and coverage of the TiO₂ film.

Huang *et al.* (2016) deposited CH₃NH₃PbI₃ perovskite thin film using a two-step ultrasonic spray coating method. In this process, they prepared first the PbI₂ thin film onto a substrate at 60°C, using PbI₂ precursor solution dissolved in DMSO, by ultrasonic spray. Secondly, in step two, the CH₃NH₃I precursor solution in isopropanol, was sprayed over the already fabricated PbI₂ film at 80°C. The prepared film was then heated to promote the interdiffusion reaction between PbI₂ and CH₃NH₃I to be crystallized in the CH₃NH₃PbI₃ film. In this way, a complete perovskite thin film was formed by a two-step ultrasonic spray coating technique. The perovskite thin-film deposition using the ultrasonic spray-coating method and current density-voltage characteristics for this technology is shown in Fig. 10.

Das *et al.* (2015) fabricated a uniform perovskite thin film to attain an outstanding PCE of 13% for PSCs using the ultrasonic spray coating technique. The ultrasonic proved its efficacy as Huang *et al.* fabricated a large-area-based CH₃NH₃PbI₃ PSCs (active area 1 cm²) by two-step ultrasonic spray coating method with PCE 13.09%. The fabricated perovskite film by an ultrasonic spray coating method can be ascribed uniform and smooth (Das *et al.*, 2015). Tait *et al.* (2016) achieved an efficiency of 11.7% for large-area-based PSCs (3.8 cm²) by ultrasonic spray coating method. The PSC composed of the MA_{0.75}FA_{0.25}PbI₃ perovskite material deposited by this technique achieved an optimum PCE of 15.61% (Uličná *et al.*, 2018).

The low-temperature processed compact film on a large area with low roughness compared to the thickness of the film on both rigid and flexible substrates is possible by this technology. Besides, the more significant grain-sized film could be obtained by this technique in which high carrier mobility with low charge recombination occurs. Moreover, the hysteresis is more negligible for the PSCs fabricated by this technique than the spin-coating and conventional spray coating techniques. Hence, ultrasonic spray coating is preferable over spin coating and traditional coating of spray technique for the uniform deposition of film over large areas.

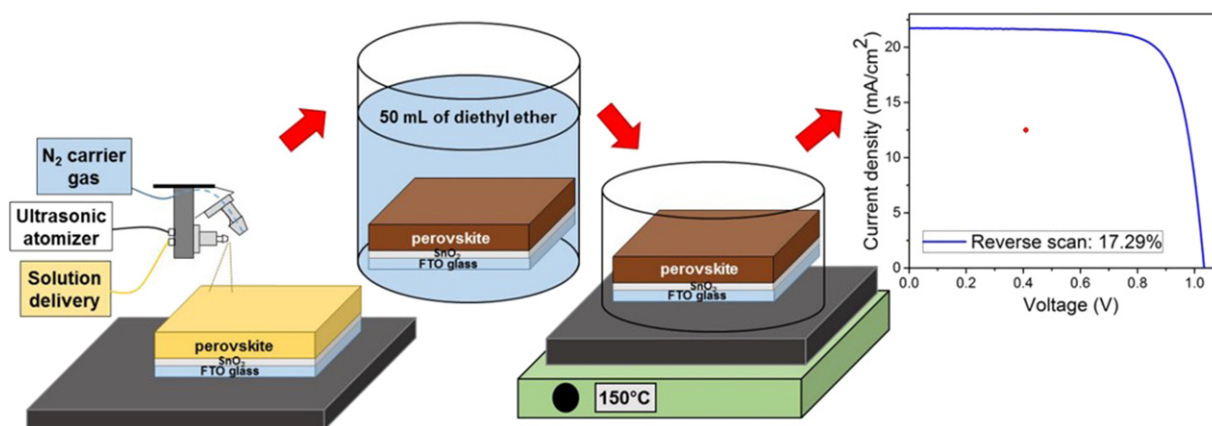


Fig. 10 Schematic illustration of an ultrasonic spray-coating technique for perovskite and corresponding Current density-voltage characteristics for ultrasonic spray-coating technology. Reproduced with permission Uličná, S., Dou, B., Kim, D.H., *et al.*, 2018. Scalable deposition of high-efficiency perovskite solar cells by spray-coating. *ACS Applied Energy Materials* 1 (5), 1853–1857. Available at: <https://doi.org/10.1021/acsaem.8b00328>. Copyright 2018, American Chemical Society.

Slot Die Coating

Another coating method, slot-die coating, is a non-contact processing method for homogeneous wet film deposition with high cross-directional uniformity and reproducibility, first invented by *Beguin (1954)* to produce photographic films and papers (*Beguin, 1954*). In slot die coating, a solution is delivered to the substrate through a fixed slot gap during the coating process, and as the substrate or die moves, a solution-based wet film is formed onto the substrate. A uniform and dry film are obtained after the evaporation or solidification of the wet film. Belonging to pre-metered coating processes, all supplied solutions are deposited on the substrate with no waste. It can handle a broad range of viscosities for the coated solution and coating speed (*Romero et al., 2006*). Krebs integrated the slot die coating process into a roll-to-roll system and showed that flexible thin films could be deposited with desired lengths, (*Krebs, 2009a,b*). The thickness of the film can be controlled by controlling the flow rate of the solution fed into the die and the coating speed (*Ding et al., 2016*).

While scaling the dimensions of large-scale PSCs, various challenges are encountered that are not found in small-area solar cells which include the need to control the morphology of perovskites over a large area to avoid the formation of pinholes or other problems that could drastically reduce the efficiency of the PSC (*Fakharuddin et al., 2014; Lin et al., 2020*). The layers in a PSC can be deposited by both one-step and two-step deposition techniques. However, one-step deposition of both the HTL and ETL layers can result in the formation of voids, resulting in faster recombination of the charge carriers. The two-step deposited perovskite films exhibit longer electron lifetime and have better morphology control over one-step deposition (*Im et al., 2014*). Thus, slot die coating is preferable for HTL and ETL depositions by two-step deposition process.

Di Giacomo et al. (2018) utilized the stripe coating capability of the process to construct series connections and parallel connections of planar structure PSCs (*Di Giacomo et al., 2018*). *Burkitt et al. (2018)* exhibited excellent performance with median PCEs of 11.74% for the slot-die-coated perovskite devices. *Hwang et al. (2015)* used an extra slot-die head connected with high-pressure N₂ to dry the PbI₂ film quickly to the original slot-die head. However, it formed a glass quenched dense PbI₂ film but was too dense to react with CH₃NH₃I, which trapped solvent inside. Therefore, the trapped solvent resulted in mobile ions forming tiny crystals, and their device showed PCE = 11.96%, with FF = 59.9%. However, the process does not seem scalable since the printed PbI₂ layer had to be stored in a small chamber to be converted to a more reactive cloudy form. The most crucial feature of this process was that the rolls used in roll-to-roll printing could be used as small chambers to bring about the cloudy PbI₂ layer. Thus, slot-die coating with gas-quenching treatment produced pinhole-free PbI₂ films. *Wu et al. (2018)* demonstrated a PCE as high as 20% for an HTL-free device architecture employing doped MAPbI₃ absorber layers. **Fig. 11** illustrates the process used by *Lee et al. (2018)* for the slot die coating technique to produce PSCs effectively. Later on, in 2020, Subbiah *et al.* developed slot-die-coated textured perovskite, 2 T-monolithic tandem solar cells with PCE of 23.8% on a 1 cm² of active area (*Moyez and Roy, 2018*).

The most striking advantage of slot die coating is the formation of highly uniform films. Its compatibility to get coupled with roll-to-roll processing, makes it even better for the large-scale production of PSCs. Thus, from all the research that has been done over the years in this field, for the future mass production of PSCs, the slot-die coating has exhibited promising prospects, and more diverse technical routes are also expected to participate in this enterprise.

Inkjet Printing

Inkjet printing is a deposition technique of a layer over a range of substrates and has been helpful in various production processes of different materials. It uses homogeneous molecular or colloidal liquid phase inks to fabricate functional layers on the substrates (*Karunakaran et al., 2019*). The inks are ejected from the nozzle in droplets and are deposited on the target substrate precisely

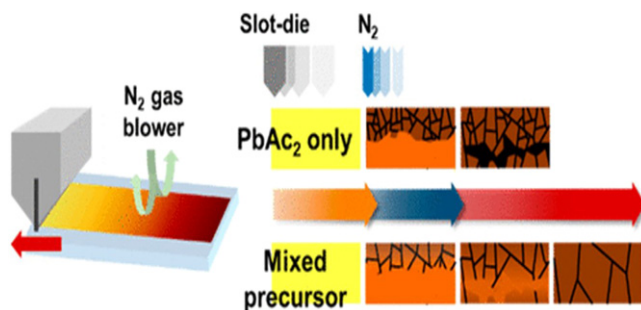


Fig. 11 Schematic illustration of slot coating technique for the production of perovskite solar cells. (Reproduced with permission Lee, D., Jung, Y.-S., Heo, Y.-J., *et al.*, 2018. Slot-die coated perovskite films using mixed lead precursors for highly reproducible and large-area solar cells. *ACS Applied Materials & Interfaces* 10 (18), 16133–16139. Available at: <https://doi.org/10.1021/acsami.8b02549>. Copyright 2018, American Chemical Society).

(Hoath, 2016; Howard *et al.*, 2019). The ink-jet printing process is a contactless and material-efficient procedure and can form a film on a flexible surface of any printed shape and thickness (Howard *et al.*, 2019). The two most common techniques used in inkjet printing nowadays are (1) continuous inkjet printing (CIP) and (ii) drop-on-demand (DOD) inkjet printing.

Continuous inkjet printing (CIP)

In this process, the fluid to be deposited gets ejected through a nozzle to form a continuous column of droplets which get systematically steered to get deposited on the intended parts of the target substrate. Rayleigh instability is used to form the droplets, which get deposited on the substrate under the influence of gravity. The most exciting feature of this process is how the droplets are steered using an electrostatic field when they come out of the nozzle. The nozzle is designed to induce a small charge on each of the droplets, which then get deflected by the electrostatic field. A piezoelectric transducer is used at the rear of the orifice to balance the flow of droplets at a suitable frequency. A typical separation can be achieved under the force of surface tension. When there is no requirement of depositing the ink on any substrate, the droplets can be deflected towards a reservoir, which collects it (Daly *et al.*, 2015). The ink can then be used for other purposes or be deposited on any other substrate. The absence of physical contact between the nozzle and the substrate is the most significant advantage of this process. Due to this characteristic, this process can deposit ink on surfaces of any morphology.

Drop-on-demand (DOD) inkjet printing

In this process, either the print head or the substrate is in motion, leading to the ink's deposition, coming out of the print head or nozzle onto the target substrate. This process is more favorable than others and is very popular due to its high placement accuracy. It also enables the generation of a single drop based on the requirements. The ink comes out of the print head due to sudden contractions in the chamber volume, which creates a pressure pulse. This pulse can be made either by using a piezoelectric transducer or the collapse of thermal bubbles, known as piezoelectric DOD and thermal DOD printing, respectively (Peng *et al.*, 2017). However, a piezoelectric transducer is favorable to control the drop size and velocity of the fluid used as the ink (Daly *et al.*, 2015).

Ink-jet printing on perovskite solar cells

Wei *et al.* (2014) first used inkjet printing to deposit a layer of carbon and MAI on a PbI_2 layer to form a thin MAPbI_3 film with better crystallinity. He then used this from planar PSCs. The fabricated devices showed $V_{oc} = 0.95$, $J_{sc} = 17.20 \text{ mA/cm}^2$, $\text{FF} = 71\%$, and $\text{PCE} = 12.3\%$ (Wei *et al.*, 2014). Later in 2018, Li *et al.* fabricated solar cells that showed a PCE of 18.6% for an area of 0.04 cm^2 , 17.7% for an area of 2 cm^2 , and $\text{PCE} = 13.3\%$ on an area of 4 cm^2 by using C_{60} as an interfacial layer between TiO_2 and MAPbI_3 (Liang *et al.*, 2018). Fig. 12 shows the inkjet printing process used by Pendyala *et al.* to fabricate high-efficiency semi-transparent PSCs (Pendyala *et al.*, 2021).

Thus, from work done over the years, it is evitable that ink-jet printing can be used to fabricate PSCs with relatively high efficiencies even on large areas, with the printing procedure being very flexible regarding thickness and structure. However, the printing speed is limited by nozzles and typically slower than other coating methods. Also, the development of suitable inks is a field that requires further improvement to achieve better-coated layers. Thus, this process has a high potential to emerge as the best deposition process of layers in PSCs.

Vapor Technology Processed Perovskite Solar Cell

Vapor deposition is the best and most efficient way to deposit excellent material layers on target substrates without any uneven morphology being developed in the layers. The material deposited in this process is converted into vapors inside a vacuum chamber by various heating processes. Thus, gradually the vapor pressure of the material increases inside the chamber, and when

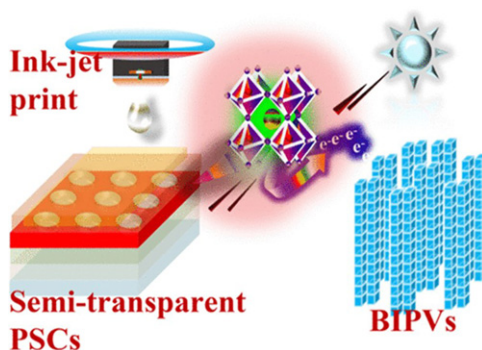


Fig. 12 Illustration of the Ink-Jet Printing Process used to fabric semi-transparent PSCs. Reproduced with permission Pendyala, N.K., Magdassi, S., Etgar, L., 2021. Fabrication of perovskite solar cells with digital control of transparency by inkjet printing. *ACS Applied Materials & Interfaces* 13 (26), 30524–30532. Available at: <https://doi.org/10.1021/acsami.1c04407>. Copyright 2021, American Chemical Society.

the value exceeds a specific limit, the vapors get deposited on the substrate, (Xie *et al.*, 2015) which is usually placed at the top of the chamber, with its active area facing downwards. Jang *et al.* illustrated a process for fabrication of PSCs using Vapor Deposition Technology (Jang *et al.*, 2019).

The process can be sub-categorized into two different processes, (1) Physical Vapor Deposition (PVD), and (2) Chemical Vapor Deposition (CVD), with the highest efficiency reported being 20.28% (Li *et al.*, 2020) and 15.6%, (Leyden *et al.*, 2016) respectively, in the deposition of the perovskite layer. Both processes involve converting the material, i.e., MAI and PbI_2 , into vapors and the subsequent deposition of the layers on the target substrate. However, there is one significant difference between the two processes. While for PVD, the coating material is in solid form, whereas in CVD it is in gaseous form.

This process has been associated with certain drawbacks, such as the need to achieve very high temperatures, highly costly precursors required, and the size limited to reaction chamber capacity. However, the vapor deposition method possesses multiple advantages over the solution-processed techniques, including high purity of the sublimed materials, precise control of the deposited film thickness, and elimination toxic solvents for thin-film formation (Solovyev *et al.*, 2014). Also, with recent improvements in the field and the advancement of technology, the benefits of the process overcompensate the drawbacks, such as the heating process can be controlled, which is either done by using an electrically resistive heat element or an Electron Beam. The consequent vapor pressure can be controlled accurately, as can be the deposition of the vapors onto the substrate using quartz crystal deposition control or any other hardware or software (Olsson *et al.*, 2000). Thus, the entire process can be computerized, leading to further improvements in the accuracy of the layer formation, thus making the process even better, thus rendering it the best process known. Another significant advantage of getting computerized is that the data can now be stored for future references in research or other applications. Thus, due to its immense potential to be used in the fabrication of PSCs, this process needs further attention and more thorough investigation in years to come.

Physical Vapor Deposition

In physical vapor deposition, required materials are deposited on target substrates, with the thickness of the layers being in the range of angstroms to microns. The material to be deposited or the source material is heated in a vacuum chamber converted into vapor. The vacuum inside the chamber facilitates the formation of a large amount of vapor even under a small amount of vapor pressure, (Campbell, 2001; Khairnar, 2014). Thus, the source material is mounted at the bottom of the chamber, and the substrate is placed at the top of the chamber, with its face down. The source material can be heated by using either an electrically resistive heat or Electron Beam to convert it into vapor, (Solovyev *et al.*, 2014; Will, 2000) This vapor then gets deposited on the substrate, placed at the top of the chamber to form the desired layer. The process usually uses quartz crystal deposition control (Liu *et al.*, 2013), or any other hardware or software for real-time deposition rate monitoring and control, thus achieving the right thickness with minimum supervision.

Thus, this process is beneficial for PSCs fabrication. Liu *et al.* used dual-source physical vapor deposition to achieve perovskite films having an average film thickness of approximately 330 nm. The use of the dual-source vapor deposition concept formed the superior uniform perovskite films over a large area and improved the performance of PV devices' performance. The solar cells thus fabricated showed an efficiency of 15.4% (Liu *et al.*, 2013). Choy *et al.* used thermal vapor deposition to form morphology controlled $\text{CH}_3\text{NH}_3\text{PbI}_3$ films using PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$ raw materials, which attained the PCE of 14.52%. PbCl_2 instead of PbI_2 was reported to release MAI as the by-product, released as vapor, thus accelerating the perovskite crystallization process (Campbell, 2001). Fan *et al.* (2016) achieved a maximum PCE of 10.9% using single-sourced physical vapor deposition using $\text{CH}_3\text{NH}_3\text{PbI}_3$ materials, which did not undergo a chemical reaction midway to the sample or the surface of the sample, thus offering high phase purity and good crystallization. Fig. 13 shows the Physical Vapor deposition process used by Costa *et al.* (2017) to fabricate PSCs. Li *et al.* (2020) deposited perovskite on the substrates by co-evaporating PbI_2 powder and MAI powder in



Fig. 13 Schematic Diagram of the deposition of the precursors of PSCs using Physical Vapor Deposition; and the electron microscopy images of the morphology of the different layers thus formed. Reproduced with permission J.C.S., Azevedo, J., Santos, L.M.N.B.F., A., Mendes, 2017. On the deposition of lead halide perovskite precursors by physical vapor method. *The Journal of Physical Chemistry C* 121 (4), 2080–2087. Available at: <https://doi.org/10.1021/acs.jpcc.6b11625>. Copyright 2014, American Chemical Society.

effusion sources, thus developing solar cells with PCE of 20.28% with an active area of 0.16 cm² and PCE of 18.13% on with an active area of 21 cm². The perovskite film was post-treated by 20 mM KAc and MAI (1:1 molar ratio) mixed solution in IPA (Solovyev *et al.*, 2014).

As is evident from all the work pursued in this case, the process of physical vapor deposition holds enormous potential for developing highly controlled, fragile layers of perovskite material on required substrates, thus fabricating high-efficiency PSCs with excellent precision. Not a lot of research has been done in this field, and therefore, it still has a lot of highly ambitious prospects in years to come.

Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a process to produce solid products using gases. It is a highly efficient vapor deposition technology for producing pinhole-free perovskite thin films on a large scale. The high material yield ratio and scalability make the CVD technique desirable for depositing perovskite layers. The reaction process of CVD mainly occurs by some methods such as vapor-based reagents generation process, reactant transport process, chemical reaction process, and reaction by-product removal process (Leyden *et al.*, 2014). The controllable variables of the chemical reaction process of this technique are pressure, deposition temperature, gas flow rate, deposition time, substrate material, and the chemicals that support the reaction (Darr *et al.*, 2004). Using CVD, Leyden *et al.* fabricated a small area methylammonium iodide (MAI) based perovskite solar cell with a PCE of 15.6% (active area = 0.09 cm²), which is the highest reported efficiency for CVD based perovskite solar cell (Will, 2000).

Perovskite film formation by CVD

In this method, perovskite layers are deposited by co-evaporation of two different precursor solutions (MAI and PbI₂) (Tavakoli *et al.*, 2015). At first, the solutions are heated. They are then mixed by chemical reaction and at last transferred to a preheated substrate TiO₂ by an inert transport gas to form a highly uniform, pinhole-free perovskite thin film with larger grain size and longer carrier lifetime. Perovskite photovoltaic thin film can be synthesized through CVD technology like Atmospheric Pressure CVD, Low-Pressure CVD, Aerosol Assisted CVD, etc.

Atmospheric pressure CVD

Atmospheric Pressure CVD or APCVD is one of the best and most promising methods to produce high-quality perovskite thin film with a large active area. This technique is promising due to its scalable vapor-growth process. The resultant modules, in this case, maintain a high steady-state power at larger areas compared to the modules grown by other techniques. In 2015, a high qualitative CH₃NH₃PbI₃ perovskite thin film was first developed by the one-step APCVD method, which obtained PCE of 11.1% (Chen *et al.*, 2015). The PSCs fabricated using the two-step sequential tubular CVD method for the first time achieved PCE within 10.29%–13.76% in the same year (Luo *et al.*, 2015b).

Low-pressure CVD

Low-Pressure CVD or LPCVD used low pressure in a high vacuum environment to deposit thin-film based on precursor solution adsorption and subsequent surface reactions. The perovskite thin film prepared by the LPCVD method exhibits a strong absorption tendency, better crystallinity, higher stability, and long carrier diffusion length. In 2015 Luo *et al.* first incorporated the LPCVD method to fabricate the perovskite thin film (Luo *et al.*, 2015a). This method fabricated efficient PSC with a PCE of 6.22% on an active area of 8.4 cm² using CH₃NH₃I and PbI₂ raw materials. The raw materials were loaded in a capped graphite boat to react at

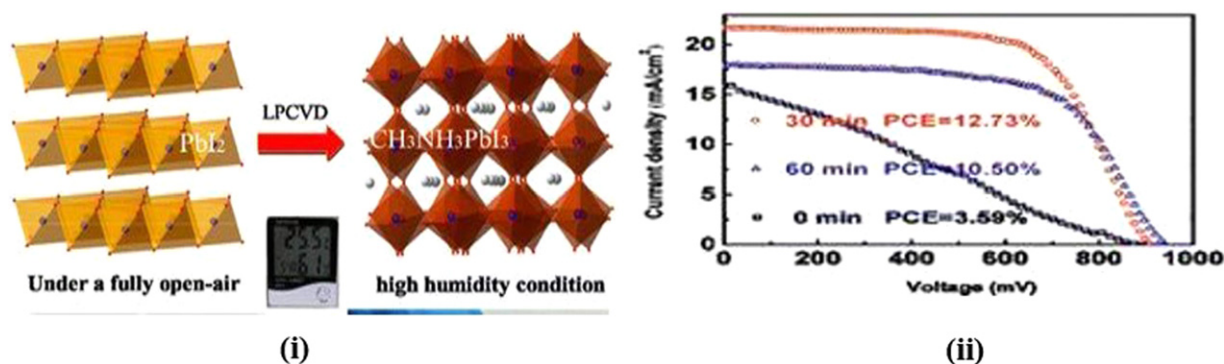


Fig. 14 (i) Schematic illustration of LPCVD technique. (ii) Current density-voltage characteristics for spray-coated perovskite solar cell. Reproduced with permission Afzaal, M., Salhi, B., Al-Ahmed, A., Yates, H.M., Hakeem, A.S., 2017. Surface-related properties of perovskite CH₃NH₃PbI₃ thin films by aerosol-assisted chemical vapour deposition. *Journal of Materials Chemistry C* 5 (33), 8366–8370. Available at: <https://doi.org/10.1039/c7tc02968c>. Luo, P., Liu, Z., Xia, W., *et al.*, 2015a. Uniform, stable, and efficient planar-heterojunction perovskite solar cells by facile low-pressure chemical vapor deposition under fully open-air conditions. *ACS Applied Materials & Interfaces* 7 (4), 2708–2714. Available at: <https://doi.org/10.1021/am5077588>.

120°C for 60 or 120 min under a pressure of 133.3 Pa. The deposition of the perovskite thin film using the LPCVD technique is shown in Fig. 14(i). The corresponding Current density-voltage characteristics for spray-coated PSCs are shown in Fig. 14(ii). Leyden *et al.* (2015) fabricated FAPbI₃ perovskite films using the LPCVD process with a pressure of 100pa and flowing dry nitrogen gas. Zhou *et al.* (2016) demonstrated an organic cation exchange concept to prepare high-quality FAPbI₃ films using this method under 10–2 Pa pressure, which achieved PCE of 2.4% with no hysteresis.

Aerosol assisted CVD

Aerosol Assisted CVD or AACVD is a highly scalable, cost-effective technique to deposit thin film than other vapor deposition methods. AACVD would be a scalable thin film formation method since it operates under ambient pressure, but this methodology requires a moderately volatile precursor. The AACVD technique was first introduced in 2014 by Lewis *et al.* to fabricate CH₃NH₃PbBr₃ thin film, (Lewis and O'Brien, 2014) and a CH₃NH₃PbI₃ film was fabricated by a two-step sequential AACVD method in next year by Binions *et al.* (Chen *et al.*, 2015). But to achieve a highly uniform, thick-enough, and smooth film, Afzal *et al.* (2017) proposed a modified three-step AACVD method in which a cold-walled horizontal-bed AACVD reactor is required to deposit the perovskite film.

Though the chemical vapor deposition technique gives excellent film quality and high PCE at a large scale, this method is costly due to the high vacuum required during the deposition which is the intrinsic drawback of this method.

Conclusion

This review discussed the more popularly known manufacturing techniques for the fabrication of PSCs, effective outside the laboratory. We started by discussing the structure of perovskites and how they made their way into being used in third-generation solar cells. With the global energy crisis gradually rising even more and the clear projection of solar energy as the major alternative source, research interest has dramatically shifted towards third-generation solar cells that are cost-effective apart from being highly efficient. Our focus in this review has been to discuss all the well-known techniques for the manufacturing PSCs, bring in the key characteristics of each technique effective in PSC production, analyze the data, and hence project the technique best suited for further production of PSCs thus deserving more research and subsequent application.

The manufacturing techniques were subdivided into two categories: solution-based and vapor technology. While solution-based processes use the liquid medium to deposit the precursors onto the substrate to form solar cells, in vapor technology, the precursors are first converted to vapor form before getting deposited onto the substrate. However, roll-to-roll techniques constitute the pathways for rendering the other manufacturing processes into industrially compatible ones.

Spin coating, which directly falls under solution-based techniques, is one of the most well-known techniques that has been the leading process for PSC development at a laboratory scale for several years now. However, if we increase the production scale even slightly, the efficiency falls drastically, thus rendering it unsuitable for fabrication outside the laboratory. Casting is an emerging technique, quite similar to spin coating. However, this process offers rapid crystallization on the substrate. Moreover, the film thickness and other effective properties mainly depend upon the solid concentration in the film and not much on the way it is deposited, thus making it better suitable for large-scale production of PSCs than spin coating.

The film prepared through the spray coating technique exhibits higher thermal stability, better optoelectronic properties due to better charge transfer capability, and higher carrier lifetime. This practical perspective makes the cheapest and fastest film-processing technique, namely the spray coating method, one of the best thin-film deposition methods. Though, in large-scale

production, the films thus deposited are not highly homogeneous, the even morphology of the film on the substrate overshadows the demerit. Ultrasonic spray coating is a relatively new technique, depositing thin films with larger grain sizes, thus achieving even higher carrier mobility with low charge recombination. Uniform film deposition can be obtained on larger areas using this technique, thus making it more preferable to conventional spray coating. Though slower than other coating processes, inkjet printing can fabricate PSCs with relatively high efficiencies even on large areas, with the printing procedure being very flexible regarding thickness and structure. However, slot die coating is the most efficient solution-based technique, coupled with roll-to-roll production. Its unique advantage of achieving highly uniform films and completely avoiding voids and pinholes in the film deposited effectively makes PSCs achieve high efficiencies even on comparatively large areas, thus making it the most suitable technique for large-scale production PSCs.

However, emerging techniques such as physical vapor deposition and chemical vapor deposition have shown significant potential for large-scale production of PSCs. Both processes give excellent film quality with high purity and high power-conversion efficiency; nevertheless, they are effectively slow and require expensive precursors. However, research trend has shown that the disadvantages can be countered effectively. But, what drives the interest of research in this field research, the processes have the added advantage of being highly controlled and compatible with various hardware and software, thus leading the production of PSCs into computerized techniques, which may be further manipulated by artificial intelligence.

Thus, among the excellent research processes of manufacturing, slot die coating, coupled with roll-to-roll technology, is one of the most effective techniques for manufacturing of PSCs and is projected to be quite close to being directly applied in industry. However, with the recent leaps in research on artificial intelligence, and computerized manufacturing of various products, the vapor deposition techniques show even more potential for developing highly efficient Perovskite solar cells on a large-scale basis. Other than these, several other processes have been developed by researchers over the years; nevertheless, none is previously known to be an industrially scalable process, and thus we have restricted our focus to the methods already discussed in this review.

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Recent Progress in Magnetoelectric Composite Thick and Thin Films

Deepak R Patil, Ajeet Kumar, and Atul Thakre, School of Materials Science and Engineering, Yeungnam University, Gyeongsan, South Korea

Dae-Yong Jeong, Department of Materials Science & Engineering, Inha University, Incheon, South Korea

Jungho Ryu, School of Materials Science and Engineering, Yeungnam University, Gyeongsan, South Korea

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Abstract

Magnetoelectric (ME) composites comprising ferromagnetic and ferroelectric phases have encouraged substantial number of research activities due to strain-driven interface coupling between two different phases. The multifunctionality of ME composites makes them potential candidates for applications in novel multifunctional devices, such as sensors, memories, and medical devices. In this review, we summarized the remarkable progress in ME composite thick/thin films performed in the most recent years. Although ME nanocomposite thin films generate comparatively weaker ME coupling voltages compared to bulk composites, they have potential applications in miniaturized ME devices, such as integrated electronics, spintronics based memory devices, and medical devices owing to their ideal interfacial coupling and volumetric/areal advantages.

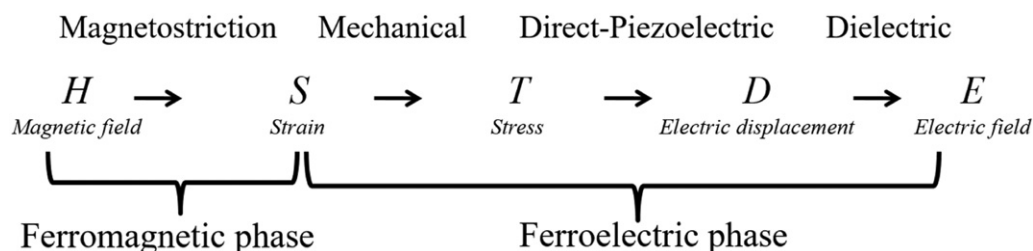
Key Points

- The interface strain plays an important role in the coupling between the magnetic and ferroelectric properties of ME composite thin films.
- The laminated composites exhibited the largest ME voltage coefficient of 50 V/cm•Oe for Metglas/PMNPT laminates at off-resonance.
- The ME voltage coefficient values for the ME nanocomposite thin films were below 1 V/cm•Oe at off-resonance.
- 2–2 type nanocomposite films are easy to fabricate and leakage current problem is also easy to mitigate in 2–2 type nanocomposite.
- 1–3 type nanocomposites mitigate substrate clamping effect, which is generally observed in 2–2 type nanocomposites and possesses very large ME coupling.
- ME composite thin films have potential application in miniaturized ME devices, such as integrated electronics, spintronic based memory devices, and medical devices.

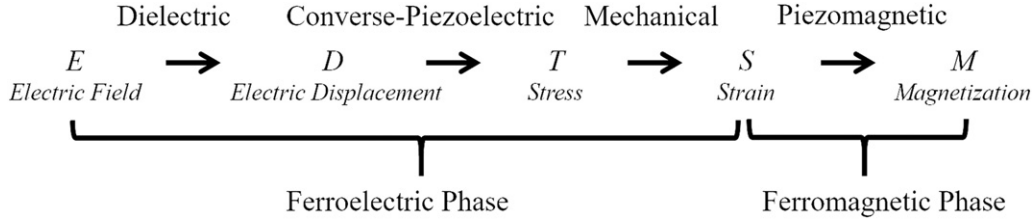
Introduction

Magnetoelectric (ME) composites composed of piezoelectric and magnetostrictive phases have gained significant interest owing to their multifunctional properties that are not present in the individual constituent phases, which open possibilities for new multifunctional devices (Nan *et al.*, 2008; Fiebig, 2005). ME composites are characterized by the ME coupling effect, which is a product property of the piezoelectric effect in the ferroelectric phase and the magnetostrictive effect in the ferromagnetic phase (Fiebig, 2005). Depending upon the external stimuli (electric field (E) or magnetic field (H)), there are two types of ME effects: direct ME effect (control of electric polarization P by applying H) and converse ME effect (control of magnetization M by applying E). The direct and converse ME effects in ME composites can be easily understood from the following mechanisms (Cho and Priya, 2011).

Direct ME effect:



Converse ME effect:



In general, the ME effect in ME composites is a strain-mediated elastic coupling between ferroelectric and ferromagnetic phases, and is strongly dependent on the microstructure of the composites and interface coupling between the two phases. In the direct ME effect, the applied magnetic field induces strain in the ferromagnetic layer through the magnetostrictive effect, which is then transferred as a stress to the ferroelectric phase, resulting in dielectric polarization change through the direct piezoelectric effect. In the converse ME effect, the applied electric field induces stress in the ferroelectric layer through the converse piezoelectric effect, which is then transferred as a strain to the ferromagnetic phase, resulting in magnetization.

Different types of ME composites have been extensively investigated owing to their ease of synthesis and device integration, and large ME coupling at room temperature (Nan *et al.*, 2008; Ma *et al.*, 2011). The most commonly known ME composites are 0–3 type particulates with magnetic phase embedded in the piezoelectric phase or vice versa (Fig. 1(a)), 2–2 type laminates with alternating layers of magnetic and piezoelectric layers (Fig. 1(b)), and 1–3 type rod/fibers composites with magnetic rods/fibers embedded in the piezoelectric matrix (Fig. 1(c)).

The 2–2 type laminate composites have high ME coupling compared to the 0–3 and 1–3 composites owing to the higher interface area between the two phases and elimination of the electric leakage problem. In addition, the 2–2 composites can be fabricated in different structures, such as unimorphs or bimorphs with multilayer structures, along with the freedom to choose different shapes and geometries. The 2–2 composites are generally fabricated by co-firing magnetic and piezoelectric ceramics or laminating them using conductive epoxy or glues. The latter provides easy control for fabrication and high performance. The high ME coupling in the composites is preliminary based on the superior physical properties of the magnetostrictive and piezoelectric phases. Therefore, the selection of suitable constituent phases plays an important role in achieving a good ME response. Some of the most commonly used magnetostrictive and piezoelectric materials are listed in Table 1 (Palneedi *et al.*, 2016a).

Fundamentals of ME Coupling

The ME coupling in composite which is described as the product of tensor property arises due to mechanical coupling between magnetostrictive and piezoelectric phases. The magnetic-field-induced ME coupling can be represented as:

$$\alpha_{ij}^H = \left(\frac{\partial P_i}{\partial H_j} \right) = \epsilon_0 \epsilon_r \left(\frac{\partial E_i}{\partial H_j} \right) = \frac{\epsilon_0 \epsilon_r \left(\frac{\partial V}{\partial H} \right)}{t} = \epsilon_0 \epsilon_r \alpha_E \quad (1)$$

where, α - ME coefficient, P -polarization (C/m²), H -magnetic field (A/m), ϵ_0 -dielectric permittivity in vacuum (8.854×10^{-12} F/m), ϵ_r -relative dielectric permittivity, E [= V/t]-electric field (V/m); V -voltage and t – thickness of piezoelectric player, and α_E -ME voltage coefficient.

α -is expressed in the unit of (sec/m) and α_E is expressed in V/cm•Oe. In general, α_E is characterized by $\alpha_E = kdq$. where, k is a coupling factor between the two phases, d is piezoelectric coefficient of piezoelectric phase and q is the piezomagnetic coefficient: $q = d\lambda/dH$ (λ is the magnetostriction) of magnetostrictive phase.

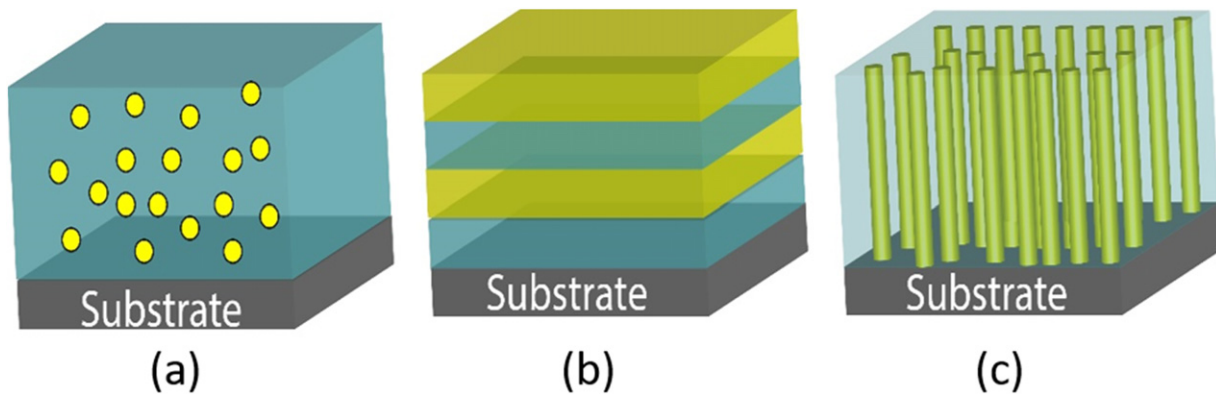


Fig. 1 Schematic of (a) 0–3, (b) 2–2, and (c) 1–3 type magnetoelectric composite nanostructures.

Table 1 List of piezoelectric and magnetostrictive materials used as constituent phases of ME composites

Piezoelectric Materials	Magnetostrictive Materials
Lead-based: $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), PbTiO_3 (PTO), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT), $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PZN-PT), $\text{b}(\text{Mg}_{1/3}\text{Nb}_{2/3})_y(\text{Zr}_x\text{Ti}_{1-x})_{1-y}\text{O}_3$ (PMN-PZT), $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PIN-PMN-PT)	Metals: Fe, Co, Ni Alloys: FeNi, CoNi, FeCo Ni_2MnGa , Galfenol (FeGa), FeGaB, Permendur (FeCoV), Samfenol (SmFe ₂) Terfenol-D ($\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$) Metallic glasses (FeBSi, FeBSiC, FeCoB, FeCoSi, FeCoSiB, FeCuNbSiB) Ferrites: Mn ferrite, Fe_3O_4 , $\text{La}_x\text{Ca}_y\text{MnO}_3$ (LCMO), $\text{La}_x\text{Sr}_y\text{MnO}_3$ (LSMO)
Lead-free: BaTiO_3 (BTO), $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BSTO), $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN), $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) AlN , ZnO (Sr, Ba) Nb_2O_5 , $\text{Bi}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST), BiFeO_3 (BFO) PVDF	

Note: Palneedi, H., Annappureddy, V., Priya, S., Ryu, J., 2016a. Status and perspectives of multiferroic magnetoelectric composite materials and applications. *Actuators* 5, 9. <https://doi.org/10.3390/act5010009>.

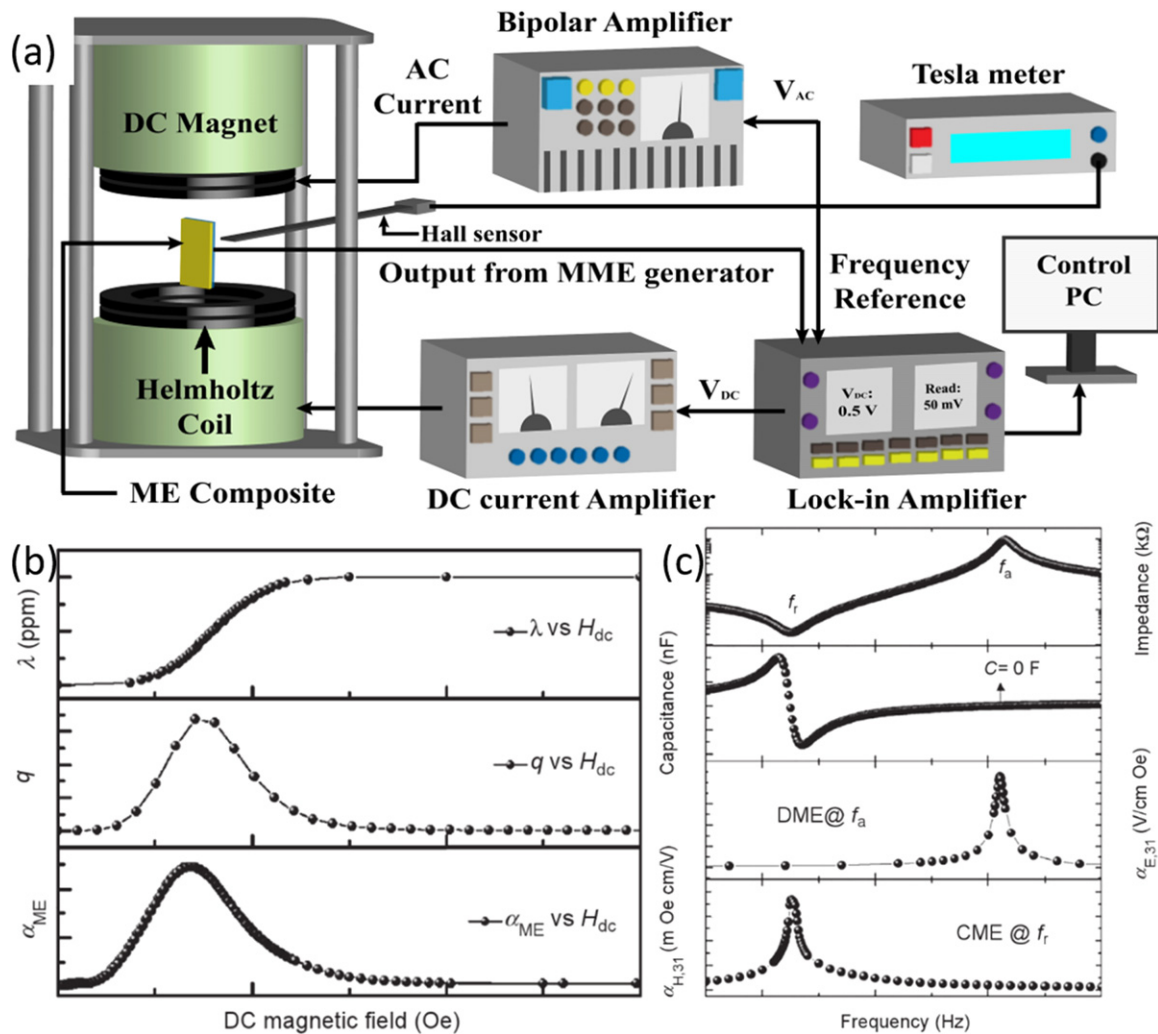


Fig. 2 (a) Experimental setup for the ME effect measurement. (b) Dc magnetic field dependent magnetostriction (λ), piezomagnetic coefficient (q), and ME voltage coefficient (α_E). Reproduced from Cho, K.H., Priya, S., 2011. Direct and converse effect in magnetoelectric laminate composites. *Appl. Phys. Lett.* 98, 232904. <https://doi.org/10.1063/1.3584863>.

The α_E is measured under two different conditions: off-resonance and resonance conditions. The most commonly used experimental setup is shown in Fig. 2(a). During measurements, the DC magnetic field (H_{dc}) and AC magnetic field (H_{ac}) are simultaneously applied. The H_{ac} is generated using a Helmholtz coil driven by a signal generator. The H_{ac} induces an AC voltage owing to the direct ME effect, which is then monitored using a lock-in amplifier. Here, the H_{ac} -induced ME voltage was studied under two different conditions. In the first condition, the H_{ac} (amplitude and frequency of the AC field) was kept constant, and α_E was measured as a function of H_{dc} . The typical behavior of α_E as a function of H_{dc} is shown in Fig. 2(b). In general, $\alpha_E(H_{dc})$ follows a qualitatively similar behavior to that of $q(H_{dc})$, which is a first-order derivative of magnetostriction, λ . Initially, α_E increased with increasing H_{dc} , reached a maximum at an optimum H_{dc} , and then decreased with decreasing H_{dc} . At high H_{dc} , α_E was negligible due to saturation of λ . The dependence of α_E on H_{dc} clearly indicates that an additional magnetic field was needed to achieve maximized α_E . In the second condition, the optimized H_{dc} (at which a higher α_E was observed) was kept constant, and α_E was measured as a function of the H_{ac} frequency (Fig. 2(c)). The α_E was 10–100 fold higher than that of the off-resonance α_E when the frequency of H_{ac} matched the electromechanical resonance (EMR) of the piezoelectric phase or the ferromagnetic resonance (FMR) of the magnetic phase in the ME composite. Cho *et al.* reported that the direct ME effect in ME composites is maximized at the anti-resonance frequency, f_a , while the converse ME effect is maximized at the resonance frequency, f_r , of the piezoelectric phase in ME composites (Cho and Priya, 2011). The position of the peak of the ME coefficient was found to be frequency-dependent capacitance of the piezoelectric phase.

Bulk ME Composites

The first bulk ME composite of $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$ (BTO/CFO) was developed in 1974 by van Suchtelen using a unidirectional solidification method (Suchtelen, 1972). They obtained an ME voltage coefficient of 0.13 V/cm•Oe at room temperature. After approximately 25 years, the Newnham's group at the Pennsylvania State University and Russian scientists reported a simple method for synthesizing bulk ME composites (Bichurin *et al.*, 1997; Harshe, 1993). They prepared various 0–3 type particulate composites of ferrites/BTO or PZT using a conventional ceramic sintering process. Subsequently, many efforts have been made to synthesize bulk ME composites with large ME voltage coefficients, which are easy to develop and cost-effective. However, the ME voltage coefficients observed for these composites were relatively low (100 mV/cm•Oe). Until the 2000 s, substantial amount of work has been done to enhance the ME coupling in particulate composites by controlling the compositions and sintering process. High voltage coefficients of approximately 10–100 mV/cm•Oe were obtained at off-resonance, while those at resonance could reach up to a few V/cm•Oe orders of magnitude. The obtained values were relatively lower than the theoretically predicted values, which could be attributed mainly to the leakage of charges due to highly conducting ferrite phases, interdiffusion between ferrite and ferroelectric phases during sintering, and thermal coefficient mismatch between the two phases during the sintering process. The problems associated with 0–3 particulate composites were eliminated by introducing 2–2 type laminate composites. In the first stage, the laminates were fabricated by co-firing the piezoelectric and ferrite layers at elevated temperatures (Srinivasan *et al.*, 2001, 2003, 2002). The laminate composites exhibited relatively higher ME voltage coefficients than the particulate composites. Ryu *et al.* reported a large ME voltage coefficient greater than

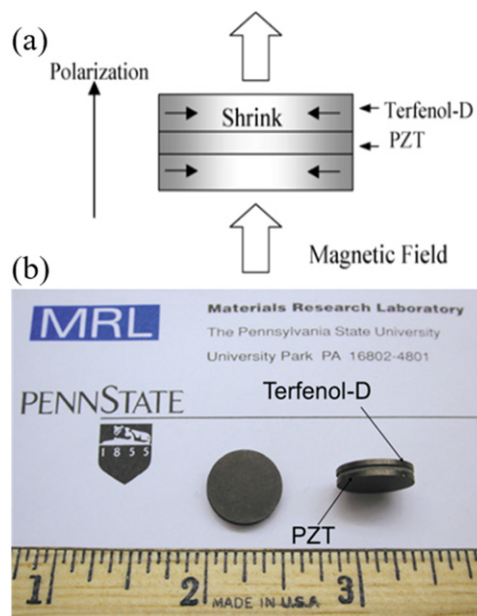


Fig. 3 ME laminate composite composed of Terfenol-D and PZT disks. (a) Schematics of the ME laminate and (b) photograph of the ME laminate. Reproduced from Ryu, J., Priya, S., Carazo, A.V., Uchino, K., Kim, H.-E., 2001. Effect of the magnetostrictive layer on magnetoelectric properties in lead zirconate titanate/terfenol-D laminate composites. *J. Am. Ceram. Soc.* 84, 2905–2908. <https://doi.org/10.1111/j.1151-2916.2001.tb01113.x>.

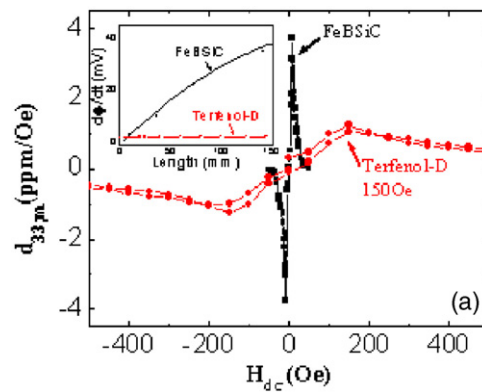


Fig. 4 Effective piezomagnetic coefficients as a function of DC magnetic bias H_{dc} for ferromagnetic FeBSiC and Terfenol-D alloys. Inset: The magnetic flux ($\delta\phi/\delta t$) as a function of the length of the ferromagnetic layer for both single FeBSiC. Reproduced from Dong, S., Zhai, J., Li, J., Viehland, D., 2006. Near-ideal magnetoelectricity in high-permeability magnetostrictive/piezofiber laminates with a (2-1) connectivity. *Appl. Phys. Lett.* 89, 252904. <https://doi.org/10.1063/1.2420772>.

4 V/cm•Oe in the ME composites of Terfenol-D laminated with PZT using conducting epoxy (Fig. 3), which introduced the potential of ME composites for technological applications in ME devices (Ryu *et al.*, 2001). Since then, a number of laminates of Terfenol-D with various piezoelectric materials, including lead-free and lead-based ceramics, single crystals, and polymers have been reported (Dong *et al.*, 2007a, 2003). The Terfenol D-based ME composites showed the strongest ME coupling; however, they are not suitable for low magnetic field applications owing to the low permeability and high saturation field of Terfenol-D.

As an alternative to Terfenol-D, few soft magnetic alloys have been reported, such as Permedur and Metglas (FeBSiC alloy) and Galfenol. In particular, Metglas-based ME composites showed relatively large ME coupling at relatively low magnetic fields (Liebermann and Graham, 1976). Metglas has a relative permeability of approximately 40,000 and saturation magnetostriction of 30 ppm at $H_{dc} \sim 10$ Oe, and exhibits a relatively higher piezomagnetic coefficient ($q = 4$ ppm/Oe) than that of Terfenol-D at low fields (Fig. 4) (Zhai *et al.*, 2006a; Dong *et al.*, 2006).

The Metglas-based ME laminates showed relatively large ME coupling for both the off-resonance and resonance. Subsequently, several advancements have been done to enhance the ME coupling in Metglas-based ME laminates by tailoring the number of layers of the Metglas, the geometry of the ME laminates, the thickness ratio of the Metglas, and the piezoelectric phase (Park *et al.*, 2009a; Fang *et al.*, 2009; Park *et al.*, 2009b; Das *et al.*, 2009). An ME voltage coefficient of 21.5 V/cm•Oe was achieved at off-resonance frequency in Metglas based ME composites. In addition to the magnetostrictive phases, different piezoelectric phases have been adopted to enhance the ME coupling in ME laminates. Different ferroelectric polymers, such as PVDF and P(VDF-TrFE), have been utilized owing to their good piezoelectric properties and showed the improved mechanical properties (Zhai *et al.*, 2006a; Jin *et al.*, 2011; Lu *et al.*, 2011). Apart from ceramics and polymers, PZT-based single crystals have gained significant interest owing to their excellent piezoelectric properties. Single crystal-based ME composites in combination with Metglas showed relatively large ME voltage coefficients at both off-resonance and resonance. Patil *et al.* introduced anisotropic ME laminates composed of Metglas and [011]-oriented $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{-PbTiO}_3$ (PMN-PT) single crystals, owing to the anisotropic piezoelectric properties of PMN-PT (Patil *et al.*, 2013). The ME laminates showed anisotropy in both sign and magnitude with a large ME voltage coefficient of 751 V/cm•Oe at resonance. They also achieved wide broadband by serially connecting three different Ni/[011]PMN-PT/Ni laminates with different volume fractions between Ni and PMN-PT (Palneedi *et al.*, 2015). This wide broadband with large ME coupling could be used as broadband energy harvesters or field sensors. Anisotropic piezoelectric single-crystal fiber composites (SFCs) were then developed and successfully used in magnetic field and mechanical vibration energy harvesters (Dong *et al.*, 2006; Wang *et al.*, 2011). In recent years, many advancements have been made in the field of ME composites. Recently, different self-biased ME composites have been introduced to eliminate the use of bulky electromagnets or permanent magnets required to apply DC bias field for optimum ME coupling. Self-biasing is achieved using (a) functionally graded ME laminates, (b) exchange-biased ME laminates, and (c) magnetostriction-hysteresis-driven ME laminates and non-linear ME laminates. Details about the different self-biasing techniques are given in the review by Zhou *et al.* (2016).

ME Composite Thick Films

Although bulk ME composites possess relatively large ME coupling, they are still far from being employed in miniaturized ME devices, such as in microelectromechanical system (MEMS)-based integrated electronics and medical applications. Another drawback is that most of the high performance 2-2 structured bulk composites are fabricated using adhesive layers, which can cause large mechanical energy transfer losses, resulting in lower ME coupling than expected (Nan *et al.*, 2008; Ma *et al.*, 2011). Therefore, some studies have focused on the synthesis of ME composite thick films. Limited efforts have been focused on the study of ME coupling in thick films. Different fabrication techniques have been used to fabricate ME composite thick films, such as tape casting, screen printing, electrophoretic deposition, and granule spray in vacuum deposition (GSV) or aerosol deposition (AD). Srinivasan *et al.* fabricated different ME

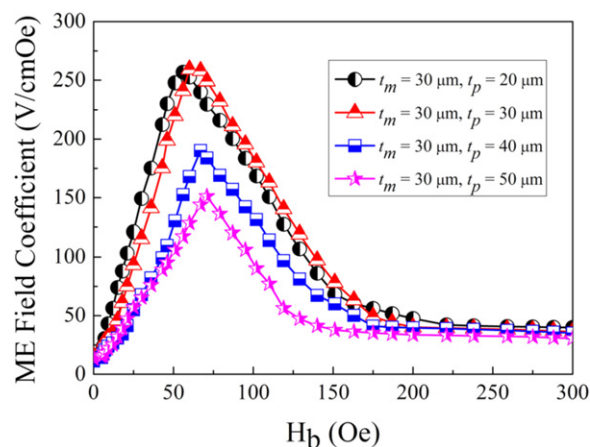


Fig. 5 The resonant ME voltage coefficient as a function of DC bias magnetic field for $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9/\text{PZT}$ thick film composites with different thickness ratios. Reproduced from Qiu, J., Gao, Y., Xu, X., *et al.*, 2017. A high-sensitivity zero-biased magnetoelectric sensor using five-phase laminate composites based on FeCoV nanocrystalline soft magnetic alloy. *AIP Adv.* 7, 056623. <https://doi.org/10.1063/1.4973944>.

composite thick films of PZT and different magnetic oxides using the doctor blade technique (Srinivasan *et al.*, 2001, 2003, 2002). They fabricated different bilayer and multilayer ME laminate composites of PZT and magnetic oxides using sintering processes at high temperatures. Most of their works was focused on determining the material parameters, working configurations, and geometries to enhance ME coupling. Patil *et al.* also reported miniaturized ME laminates (MELs) of BaTiO_3 and NiFe_2O_4 with a layer thickness of 15–50 μm (Patil *et al.*, 2011). The MELs were also fabricated using the tape casting method. However, the fabricated multilayer composites require relatively high temperatures (over 1200 $^\circ\text{C}$, in general) for the sintering of the composite, which could result in interdiffusion/chemical reactions at the interfaces, thereby resulting in the loss of ME coupling. Qiu *et al.* reported $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9/\text{PZT}$ thick-film composites with an excellent magnetoelectric (ME) coupling effect (Qiu *et al.*, 2017). Thick films were fabricated using a low-temperature electrostatic spray deposition (ESD) process. They fabricated ME thick films with different thickness ratios between FeCuNbSiB and PZT and observed a relatively large ME voltage coefficient of 259 $\text{V}/\text{cm}\cdot\text{Oe}$ at resonance (Fig. 5) (Qiu *et al.*, 2017). Chen *et al.* reported the ME effect in polyvinylpyrrolidone (PVP)-assisted CFO/PZT multiferroic thick films, which were fabricated using hybrid sol-gel processing and spin coating (Chen *et al.*, 2009). Bush *et al.* reported layered thick-film composites containing PZT and NZF screens printed on a ceramic alumina oxide substrate with a contact layer (Bush *et al.*, 2010). They achieved ME conversion factors of 57 kV/mT at low frequencies and 2000 kV/mT at mechanical resonance.

Major work on ME thick films was performed by Ryu *et al.* at the Korea Institute of Materials Science (KIMS) in Korea (Palneedi *et al.*, 2015, 2017a; Kambale *et al.*, 2013). They introduced a new technique for the synthesis of 2–2 and 3–2 type ME composites called granule spray in vacuum (GSV) or aerosol deposition (AD). The AD process is an important room temperature deposition process for fabricating condensed thick films of ceramics with nanoscale crystallite structures, which have excellent material properties and are cost effective. They fabricated 3–2 type highly dense ME composite films of $0.9\text{Pb}(\text{Zr}_{57}\text{Ti}_{43})\text{O}_3$ – $0.1\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZT–PMnN) and $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ (NZF) on platinized Si substrates using AD (Ryu *et al.*, 2012). They fabricated different ME films by varying the NZF composition from 15% to 30% and the film thickness from 10 to 30 μm . An ME voltage coefficient of 150 $\text{mV}/\text{cm}\cdot\text{Oe}$ was observed for the 20% NZF-added film. Similarly, they fabricated 2–2 type ME laminates by depositing PZT-based films on CFO sintered ceramic using AD. The dense PZT films (20 μm) showed good adhesion to the sintered CFO ceramic substrate without any cracks. They obtained a relatively large ME voltage coefficient of 130 $\text{mV}/\text{cm}\cdot\text{Oe}$. Kambale *et al.* (2013) fabricated 20- μm thick PZT films on a magnetostrictive Ni substrate using AD. They used the ceramic electrode of LaNiO_3 (LNO) as a bottom electrode for effective stress transfer from Ni to PZT and as an interdiffusion barrier. The PZT/LNO/Ni ME thick film showed a colossal ME voltage coefficient of 1 $\text{V}/\text{cm}\cdot\text{Oe}$ at off-resonance and 8.5 $\text{V}/\text{cm}\cdot\text{Oe}$ at resonance.

However, the piezoelectric thick films fabricated in the abovementioned studies require high-temperature thermal annealing ($> 600\text{ }^\circ\text{C}$) for better performance, which was achieved using conventional furnaces. Unfortunately, furnace annealing is not suitable for magnetostrictive metals or alloys due to the crystallization and oxidation of alloys, which causes degradation of magnetostrictive properties. To circumvent this problem, they adopted localized annealing of AD films on metal alloys using laser radiation. Palneedi *et al.* have recently reported laser (CW, Yb laser laser radiation (560 nm, 220 mW, 0.05 mm s^{-1})) annealing of PZT films deposited on Metglas using AD (Palneedi *et al.*, 2016b). They successfully laser-annealed 2- μm thick PZT films on Metglas (Fig. 6(a)). The laser annealing resulted in the enhancement of the dielectric, ferroelectric, and ME coupling of the ME thick films. They found an increase in the ME voltage coefficient with increasing laser energy. A maximum ME voltage of 880 $\text{mV}/\text{cm}\cdot\text{Oe}$ was obtained for a laser fluence of 345 J/mm^2 (Fig. 6(b)).

Similarly, they studied the effect of laser annealing on PZT/Metglas thick films with varying PZT thicknesses (2–11 μm) (Palneedi *et al.*, 2016b). The ME voltage coefficient showed a strong dependence on the PZT thickness based on the extent of PZT film annealing using laser radiation. A large ME voltage coefficient of 7 $\text{V}/\text{cm}\cdot\text{Oe}$ was obtained for the PZT/Metglas ME film with a PZT thickness of 6 μm (Fig. 7).

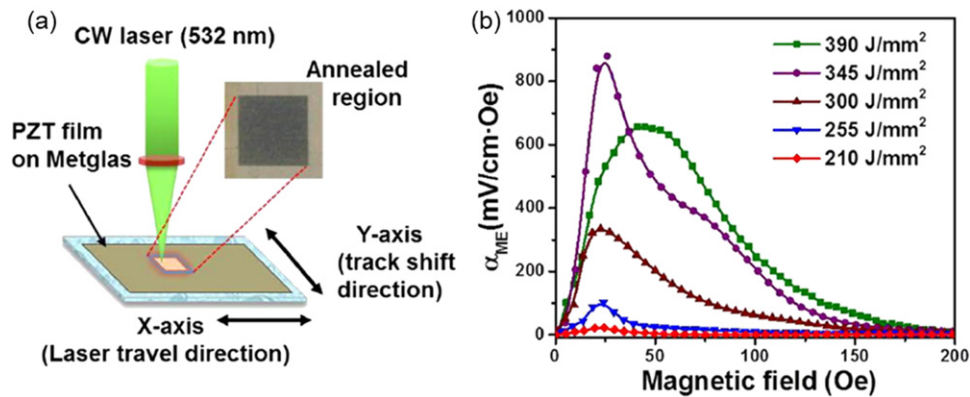


Fig. 6 (a) Schematic of laser-annealing of PZT/Metglas. (b) Variation of ME voltage coefficient (α_{ME}) as a function of H_{dc} at a fixed AC magnetic field of 1 Oe and $f = 1$ kHz for laser-annealed PZT/Metglas. Reproduced from Palneedi, H., Choi, I., Kim, G.-Y., *et al.*, 2016b. Tailoring the magnetoelectric properties of Pb(Zr,Ti)O₃ film deposited on amorphous metglas foil by laser annealing. *J. Am. Ceram. Soc.* 99, 2680–2687. <https://doi.org/10.1111/jace.14270>.

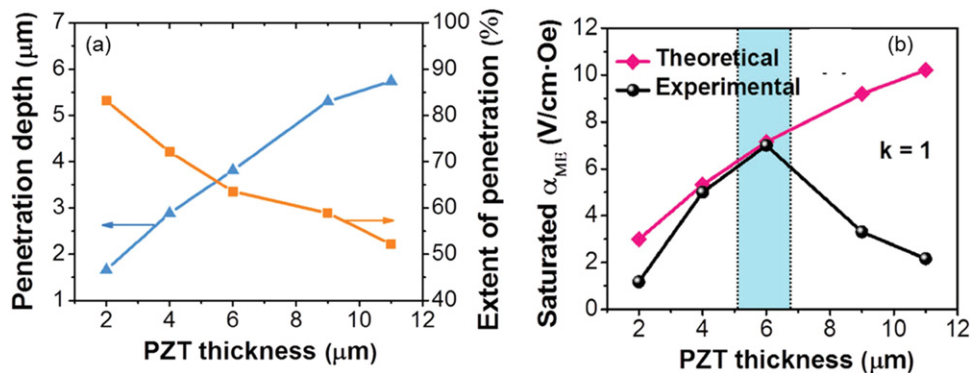


Fig. 7 (a) Variation of the laser penetration depth and extent of penetration as a function of PZT film thickness. (b) Effect of PZT film thickness on theoretical and experimental α_{ME} values. Reproduced from Palneedi, H., Choi, I., Kim, G.-Y., *et al.*, 2016b. Tailoring the magnetoelectric properties of Pb(Zr,Ti)O₃ film deposited on amorphous metglas foil by laser annealing. *J. Am. Ceram. Soc.* 99, 2680–2687. <https://doi.org/10.1111/jace.14270>.

They also fabricated self-biased ME composite thick films by depositing 4- μm thick PZT film on a 50- μm thick flexible Ni foil using AD (Fig. 8(a) and (b)). The PZT film was successfully annealed using a continuous-wave of 560 nm ytterbium fiber laser. The laser annealing resulted in an improvement in crystallinity, which led to enhanced dielectric and ME properties of the PZT/Ni ME thick films (Fig. 8(c)). They obtained a relatively high self-biased ME response of 3.15 V/cm·Oe, which was 2000% higher than that of the deposited PZT/Ni sample (Fig. 8(d)) (Palneedi *et al.*, 2018).

ME Composite Thin Films

Although bulk and thick film ME composites possess ideal ME coupling, they still have some inherent limitations such as their bulky nature, imperfect interface coupling, and sintering problems. Recent developments in thin-film fabrication techniques have motivated the researcher to fabricate different thin film ME composites. The ME composites thin films have more superiorities than bulk ME composites. The ferroelectric and magnetic phases can be combined together at the atomic scale to achieve good control of the interfacial characteristic, which are beneficial for the strain-mediated ME composites (Ma *et al.*, 2011). In this context, different types of nanostructures such as 0–3 type particulate films, 1–3 type vertical heterostructures and 2–2 type laminate heterostructures (Fig. 1) were fabricated using different growth techniques, such as Pulsed laser deposition (PLD), Molecular beam epitaxy (MBE), Metal organic chemical vapor deposition (MOCVD), spin coating, and sputtering. Spin coating is very a well-known inexpensive chemical method for fabricating polycrystalline thin films. However, epitaxial growth techniques (PLD, MBE, and sputtering) are more feasible for fabricating oxide thin films with single crystalline or self-assembled heterostructures. They provide more control over the structures at the atomic level with better elastic coupling between the two phases. Different nanocomposite thin films containing BTO, PTO, PZT, and BFO as ferroelectric phases and CFO, NFO, and LCMO as magnetic phases were prepared.

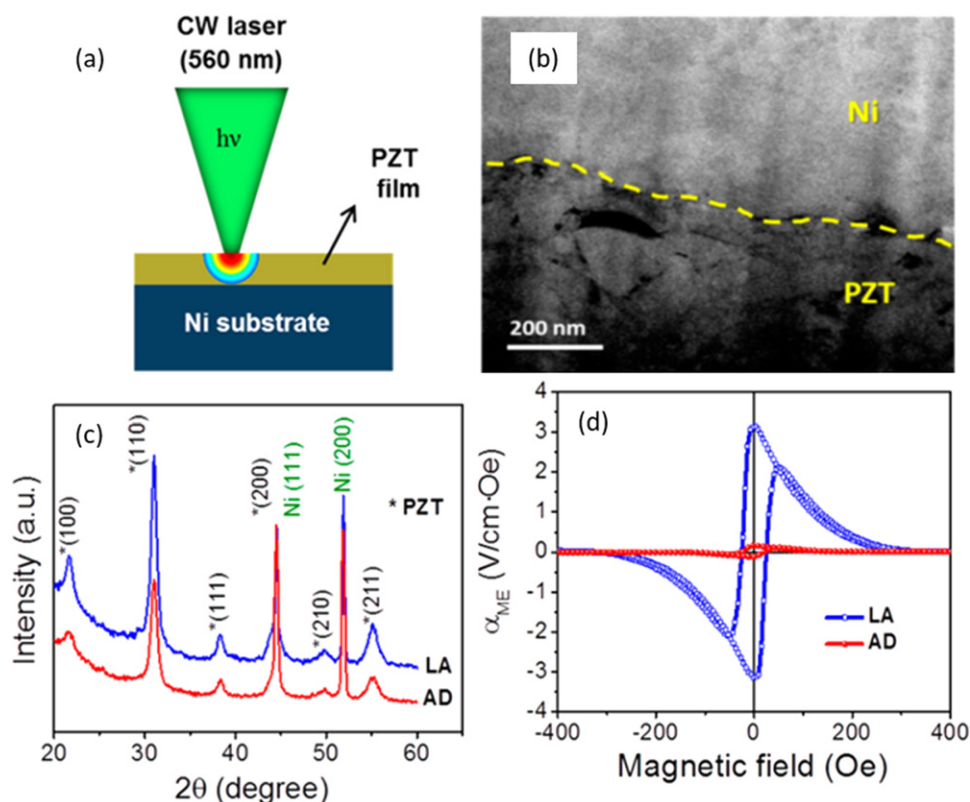


Fig. 8 (a) Schematic of laser annealing of PZT thick film on Ni substrate. (b) Cross-sectional TEM micrograph, (c) XRD pattern, and (d) ME response of the PZT/Ni thick film. Reproduced from Palneedi, H., Maurya, D., Geng, L.D., *et al.*, 2018. Enhanced self-biased magnetoelectric coupling in laser-annealed Pb(Zr,Ti)O₃ thick film deposited on Ni foil. *ACS Appl. Mater. Interfaces* 10, 11018–11025. <https://doi.org/10.1021/acsami.7b16706>.

0–3 Type Particulate Composites

The study of ME coupling in 0–3 type particulate composite thin films is very limited. 0–3 type ME thin films can be prepared using different physical and chemical deposition methods. Wan *et al.* synthesized CFO-PZT thin films with CFO nanoparticles dispersed in a PZT matrix using the sol-gel method (Wan *et al.*, 2005). They found local phase separation of the CFO and PZT phases after annealing the composite films at 650 °C (Fig. 9(a)). The films exhibited excellent electric and magnetic properties. They studied the ME voltage coefficient as a function of bias magnetic fields at different frequencies. A maximum ME voltage coefficient of approximately 317 mV/cm·Oe was obtained at a frequency of 50 kHz (Fig. 9(b)).

Similarly, NFO embedded in PZT 0–3 type nanocomposite films were prepared on Nb:STO substrates, and ME coupling in both the longitudinal and transverse configurations were studied. A maximum α_{ME} of 16 mV/cm·Oe was at frequency of 194 Hz (Ryu *et al.*, 2006). A smaller value observed for the nanocomposites was attributed to the substrate clamping effect. Zhong *et al.* fabricated 0–3 type nanocomposites of Bi_{3.15}Nd_{0.85}Ti₃O₁₂ and CFO on Pt/Ti/SiO₂/Si(100) substrates using a chemical solution deposition technique (Zhong *et al.*, 2007). The nanocomposites showed excellent ferroelectric and magnetic properties and distinct ME coupling at room temperature. Roy *et al.* reported sol-gel synthesized 0–3 nanocomposite thin films of CFO and Pb_{0.85}La_{0.15}TiO₃ with different CFO volume contents (Roy *et al.*, 2011). They reported a large α_{ME} of 250 mV/cm·Oe for 8 vol% of CFO. Cheng *et al.* successfully fabricated La_{0.6}Ca_{0.4}MnO₃-Bi_{0.6}Nd_{0.4}TiO₃ ME composite thin films grown on Pt/Ti/SiO₂/Si(100) substrates using chemical solution deposition (Cheng *et al.*, 2012). McDannald *et al.* reported electric and ME coupling in CFO/PZT nanocomposite thin films (McDannald *et al.*, 2013a). The 0.1% embedded CFO composites exhibited the highest α_{ME} of 549 mV/cm·Oe at a frequency of 1 kHz. Li *et al.* (2015) reported the fabrication of CFO/BFO 0–3 type quasi nanocomposites derived from 2–2 and 1–3 type composite layers using PLD. They proposed that this structure can significantly suppress leakage current and reduce clamping effect. They obtained a lateral ME coefficient of 338 mV/cm·Oe. Li *et al.* fabricated a novel quasi 0–3 nanocomposites of CFO-BFO using double-target PLD (Li *et al.*, 2016). They found magnetic field-induced ferroelectric switching using piezoresponse force microscopy (PFM) technology. The changes in both the amplitude and phase of ferroelectricity demonstrated the strain-mediated ME coupling effect in CFO-BFO nanocomposites. McDannald *et al.* also reported the fabrication of CFO/PZT nanocomposite thin films using a mixed precursor solution method (McDannald *et al.*, 2017). They confirmed the separation of CFO particles (25 nm) in a PZT matrix using scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) mapping techniques. They found that the discrete distribution of the CFO particles helped to mitigate leakage currents, resulting in significant remnant ME coupling. Relatively high ME voltage coefficients of 3.07 V/cm·Oe and 25 V/cm·Oe were achieved at 1 and 90 kHz, respectively.

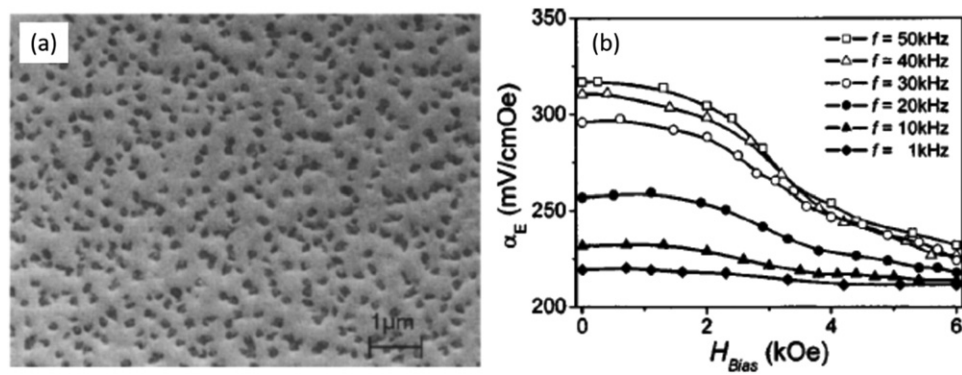


Fig. 9 (a) SEM image of the CFO/PZT nanocomposite thin film. (b) Variations of ME voltage coefficient as a function of H_{bias} at various magnetic frequency, f for the CFO/PZT nanocomposite thin film. Reproduced from Wan, J.G., Wang, X.W., Wu, Y.J., *et al.*, 2005. Magnetoelectric CoFe₂O₄-Pb(Zr,Ti)O₃ composite thin films derived by a sol-gel process. Appl. Phys. Lett. 86, 1–3. <https://doi.org/10.1063/1.1889237>.

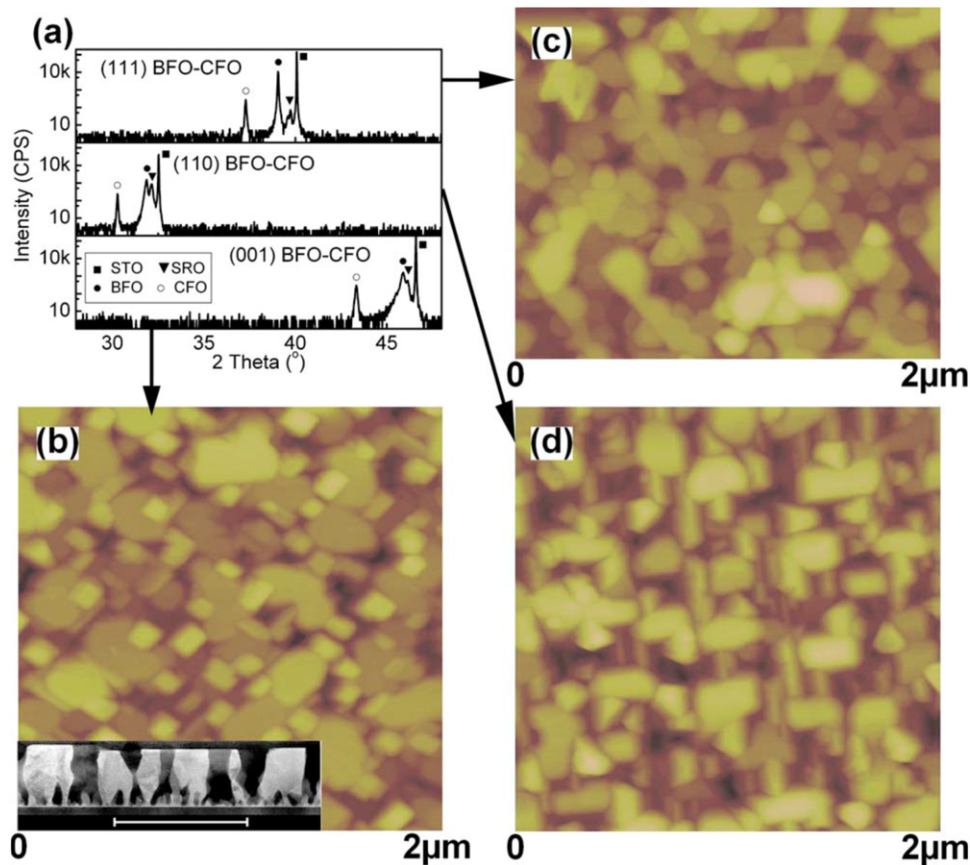


Fig. 10 (a) XRD pattern and (b,c,d) AFM image for (001), (110), and (111) BFO-CFO thin films. Reproduced from Yan, L., Wang, Z., Xing, Z., Li, J., Viehland, D., 2010. Magnetoelectric and multiferroic properties of variously oriented epitaxial BiFeO₃-CoFe₂O₄ nanostructured thin films. J. Appl. Phys., 107, 064106. <https://doi.org/10.1063/1.3359650>.

1–3 Type Vertically Aligned Nanocomposites Films

The 1–3 type vertically aligned nanocomposites consist of a magnetic phase vertically embedded into the ferroelectric matrix, or vice versa. The 1–3 type nanocomposites were designed to mitigate the substrate clamping effect by enhancing the vertical interface. A theoretical study predicted an ME voltage coefficient of up to 2 V/cm•Oe for vertically aligned nanocomposite films. The first 1–3 type composite was reported by Zheng *et al.* in 2004 (Zheng *et al.*, 2004). They grew an array of CFO nanopillars with diameters ranging from 20 to 30 nm in a BTO matrix using PLD. Transmission electron microscopy (TEM) images confirmed the formation of

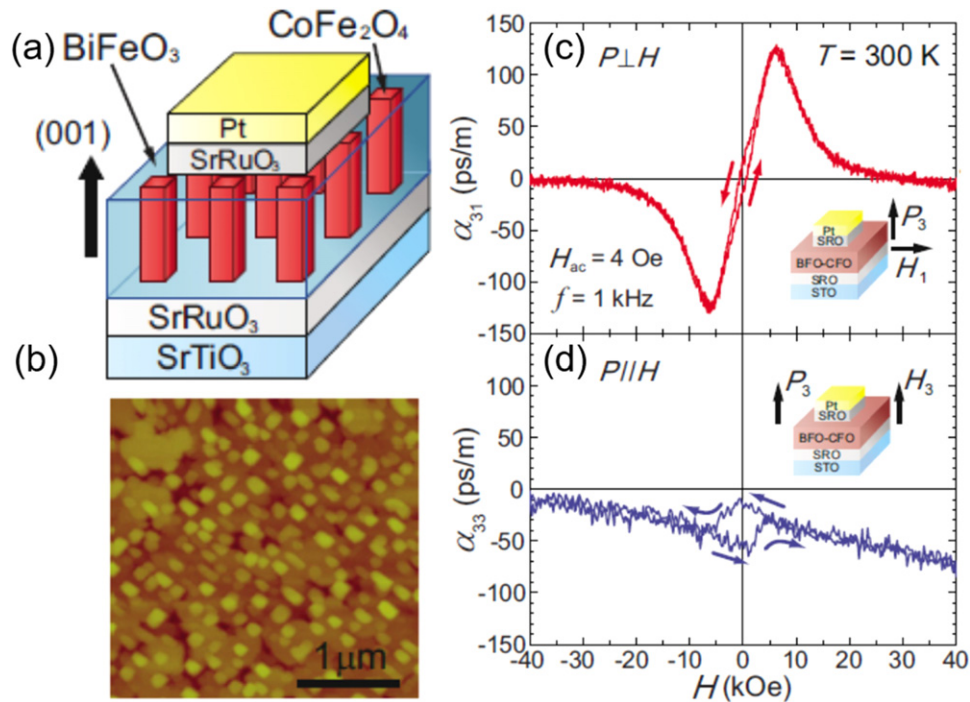


Fig. 11 (a) Schematic picture and (b) AFM image of the BFO–CFO nanocomposites. (c) Transverse ME coefficient and (d) longitudinal ME coefficient of the BFO–CFO nanocomposites. Reproduced from Oh, Y.S., Crane, S., Zheng, H., 2010. Quantitative determination of anisotropic magnetoelectric coupling in BiFeO₃–CoFe₂O₄ nanostructures. Appl. Phys. Lett. 97, 052902. <https://doi.org/10.1063/1.3475420>.

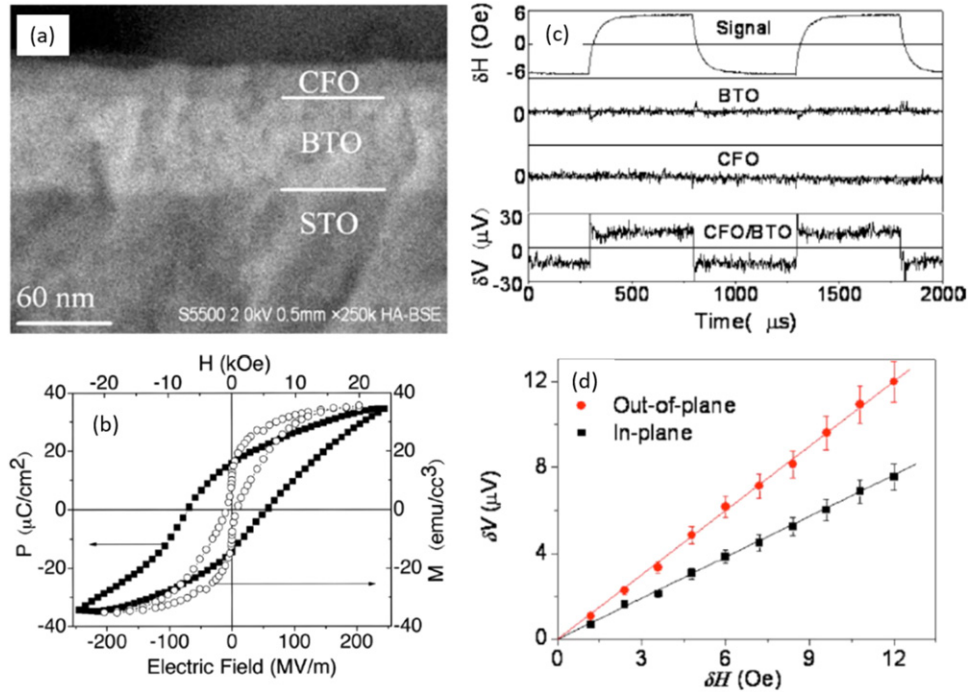


Fig. 12 (a) A cross-sectional SEM image of the heterostructured CFO/BTO composite films. (b) Ferroelectric hysteresis loop and in-plane magnetic hysteresis loop of the CFO/BTO heterostructured films. (c) The ME response of the films when the in-plane magnetic field is applied. (d) Induced ME voltage as a function of ac magnetic field δH at 1 kHz with a bias magnetic field of 100 Oe. Reproduced from Zhang, Y., Deng, C., Ma, J., Lin, Y., Nan, C.W., 2008a. Enhancement in magnetoelectric response in Co Fe₂O₄–BaTiO₃ heterostructure. Appl. Phys. Lett. 92, 062911. <https://doi.org/10.1063/1.2841048>.

25 nm diameter CFO nanopillars in the BTO matrix. The nanocomposites showed well-defined P-E loops with a saturation polarization of $23 \mu\text{C}/\text{cm}^2$ and uniaxial magnetic anisotropy with an out-of-plane easy axis. A sizable magnetization change was observed close to the ferroelectric critical temperature of the BTO, which led to significant ME coupling. Zavaliche *et al.* investigated converse ME coupling in electrically poled BFO-CFO nanocomposites using magnetic force microscopy (MFM) (Zavaliche *et al.*, 2005). Yan *et al.* reported the direct ME effect in BFO-CFO nanocomposites deposited on conductive $\text{SrRuO}_3/(001)$ STO substrates using a magnetic cantilever method, and they found the maximum ME coefficient of $18 \text{ mV}/\text{cm}\cdot\text{Oe}$ (Yan *et al.*, 2009). Similarly, they studied the ME properties in variously-oriented epitaxial BFO-CFO nanostructured films deposited on (001), (110), and (111) STO substrates (Fig. 10). They found that the electric and magnetic properties of the nanocomposites were dependent on the substrate orientation (Yan *et al.*, 2010). Oh *et al.* investigated ME coupling in two different magnetic field orientations (longitudinal and transverse ME voltage coefficients) in 300 nm thick BFO-CFO nanocomposite thin films under a small AC magnetic field of 4 Oe (Oh *et al.*, 2010). A self-assembled epitaxial BFO-CFO film with a thickness of 300 nm was grown on a (001) SRO/STO substrate using pulsed laser deposition (Fig. 11(a) and (b)). The transverse ME voltage coefficient ($60 \text{ mV}/\text{cm}\cdot\text{Oe}$) was found to be five times larger than the longitudinal ME voltage coefficient owing to the enhanced transverse magnetostriction of the CFO nanopillars (Fig. 11(c) and (d)). Tang *et al.* (2019) reported the fabrication of 1-3 type BTO-NZFO nanocomposite thin films via a simple 0-3 composite fabrication process. They controlled the orientation of NZFO nanocrystals in BTO using magnetron sputtering and studied their effect on ME coupling. Basov *et al.* reported a new strategy to grow 1-3 type ME nanocomposites using an alumina layer template for the growth of free-standing vertically aligned CoFe_2 nanopillars using a pulsed electrodeposition method (Basov *et al.*, 2017). BSTO-CFO nanocomposites were grown by depositing BSTO on CFO nanopillars using radio frequency. The large interfacial area between BSTO and CFO resulted in a relatively large ME voltage coefficient of $320 \text{ mV}/\text{cm}\cdot\text{Oe}$.

Recently, Cheng *et al.* investigated direct ME coupling in BTO-CFO nanocomposite thin films using a PFM amplitude mapping study (Chen *et al.*, 2019). The discrepancy between the butterfly loops under zero and 2 kOe magnetic field confirmed the presence

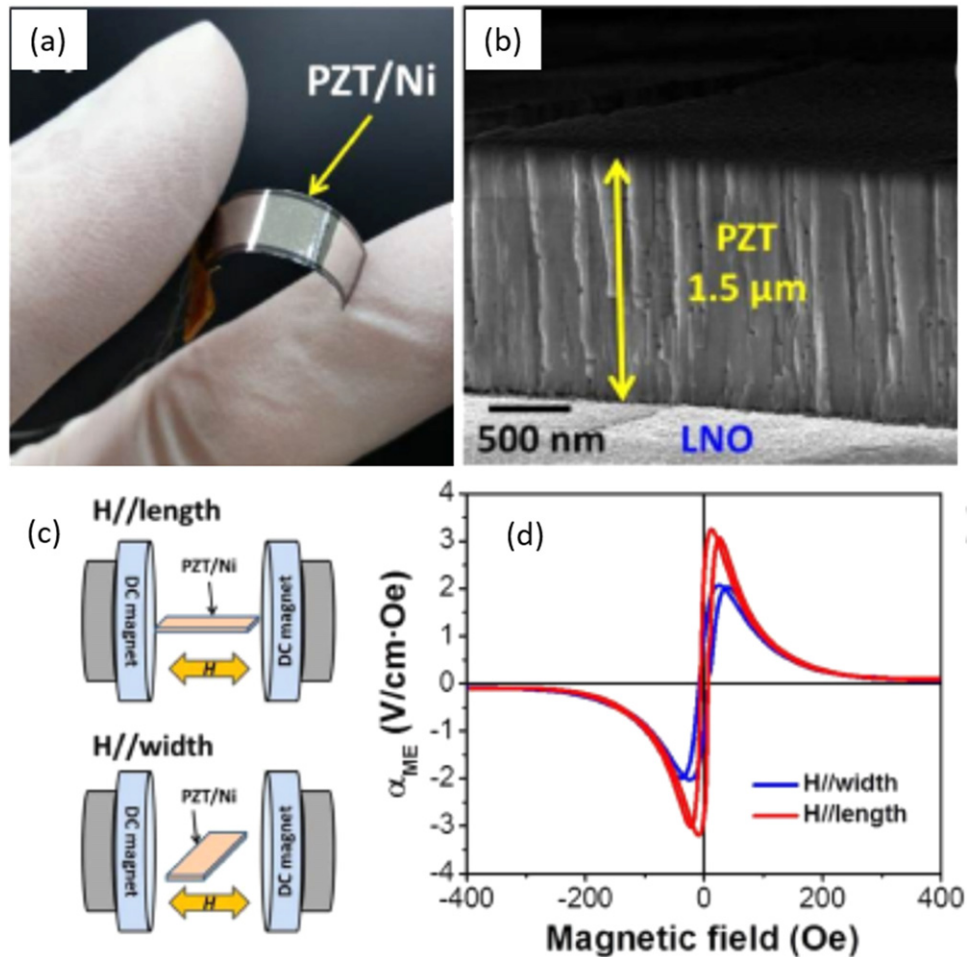


Fig. 13 (a) Prototype of flexible PZT/Ni ME composite. (b) Cross-sectional FESEM image of the PZT film. (c) Schematics of the ME measurement of the PZT/Ni sample with DC bias applied along its length and width directions, (b) H_{bias} dependence of ME for the PZT/Ni composite. Licensed under a Creative Commons Attribution (CC BY) license. Reproduced from Duan, Z., Fu, X., Mei, Y., *et al.*, 2020 Annealing heating rate dependence of microstructure and multiferroic properties in $\text{Bi}_4\text{Ti}_2.9\text{Fe}_{0.1012}\text{CoFe}_2\text{O}_4$ layered magnetoelectric composite films prepared by chemical solution deposition method. *Ceram. Int.* 46, 15654–15664. <https://doi.org/10.1016/j.ceramint.2020.03.115>.

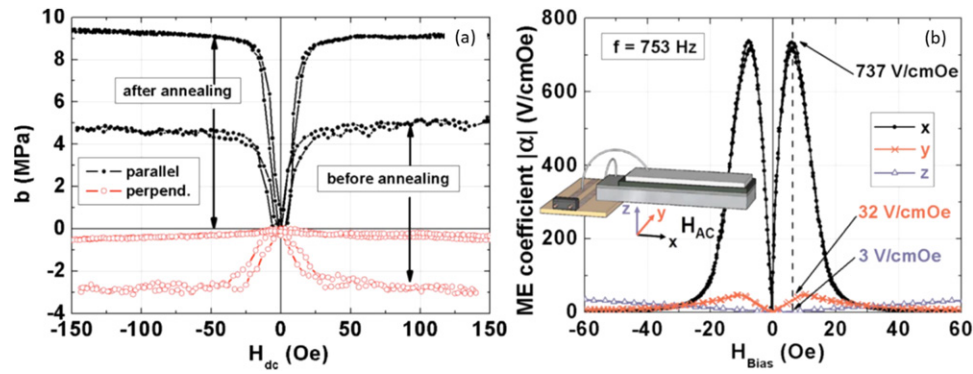


Fig. 14 (a) ME coupling coefficient of Si cantilever covered with AlN and Metglas films, as deposited and after magnetic field annealing. (b) Absolute value of the ME voltage coefficient at the resonance frequency of 753 Hz. Reproduced from Palneedi, H., Yeo, H.G., Hwang, G.T., *et al.*, 2017b. A flexible, high-performance magnetoelectric heterostructure of (001) oriented Pb(Zr_{0.52}Ti_{0.48})O₃ film grown on Ni foil. *APL Mater.* 5, 096111. <https://doi.org/10.1063/1.4993239>.

of direct ME coupling with an ME voltage coefficient of 390 mV/cm•Oe, which was higher than previously reported values. In addition, many other 1–3 type nanocomposite thin films, such as PTO-CFO, (Chen *et al.*, 2019; Tan *et al.*, 2009; Wan *et al.*, 2007) BFO-MgFe₂O₄, (Kim *et al.*, 2013) and Sr(Ti_{1-x}Fe_x)O₃-CFO, (Kim *et al.*, 2017) have been widely investigated over the years.

2–2 Type Layered Thin Films

2–2 layered structures exhibit weak ME coupling in comparison with 1–3 type nanostructures and comparable ME coupling with 0–3 type nanostructures due to substrate clamping effects. However, 2–2 layered structures are relatively easy to fabricate. In addition, leakage current is also easy to mitigate in 2–2 layered structures due to the insulating nature of the ferroelectric layers. Different 2–2 layered nanocomposite films consisting of magnetic oxides (CFO, NFO, and LSMO) and ferroelectrics (BTO, PZT) were fabricated using PLD and sol-gel spin coating techniques. The films showed relatively good ferroelectric and magnetic properties, which indicate ME coupling. Zhang *et al.* investigated ME coupling in CFO-BTO and CFO/NFO bilayer nanocomposite films deposited on STO substrates (Fig. 12(a)) (Zhang *et al.*, 2008a). As shown in Fig. 12(b), no ME signal was observed for pure BTO and CFO under an in-plane AC magnetic field. However, the CFO-BTO heterostructure shows a clear change in the output ME voltage following the on/off state of the AC magnetic field (Fig. 12(c)). The estimated out-of-plane and in-plane ME voltage coefficients were approximately 104 and 66 mV/cm•Oe, respectively (Fig. 12(d)). Similarly, Wang *et al.* fabricated BTO thin films directly on CFO, which showed an ME voltage coefficient of approximately 38 mV/cm•Oe (Wang *et al.*, 2008).

Zhang *et al.* reported a 2–2 heterostructure of CFO/BTO thin films grown on a (001) STO substrate with an ME coefficient of approximately 66 mV/cm•Oe (Zhang *et al.*, 2008a). To relax the substrate clamping effect and enhance ME coupling, He *et al.* fabricated PZT/CFO bilayers with LNO as the buffer layer and bottom electrode (He *et al.*, 2009). Similarly, Feng *et al.* synthesized PZT/Ni films on Ni foil and obtained a relatively large ME voltage coefficient of 772 mV/cm•Oe (Feng *et al.*, 2015). Liang *et al.* reported ME coupling in La_{1.2}Sr_{1.8}Mn₂O₇/PbZr_{0.3}Ti_{0.7}O₃ 2–2 type heterostructures grown on an SRO substrate (Liang *et al.*, 2017). They observed a maximum ME voltage coefficient of 17.7 mV/cm•Oe at 120 K under a magnetic field of 4.5 kOe. Mundy *et al.* reported ferroelectricity and magnetic ordering near room temperature within (LuFeO₃)/(LuFe₂O₄) superlattices (Mundy *et al.*, 2016). Gupta *et al.* prepared layered ME thin films by depositing a PZT layer on a Ni substrate using PLD (Gupta *et al.*, 2017). The

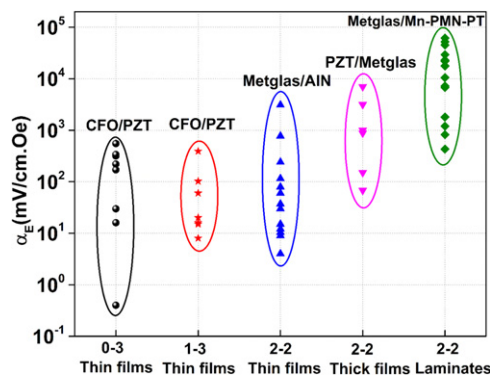


Fig. 15 Off resonance ME voltage coefficients of different types of ME composites. Reproduced from Dong, S., Zhai, J., Li, J., Viehland, D., 2006. Near-ideal magnetoelectricity in high-permeability magnetostrictive/piezofiber laminates with a (2-1) connectivity. *Appl. Phys. Lett.* 89, 252904. <https://doi.org/10.1063/1.2420772>. Jin, J., Lu, S.-G., Chanthad, C., *et al.*, 2011. Multiferroic polymer composites with greatly enhanced magnetoelectric effect under a low magnetic bias. *Adv. Mater.* 23. <https://doi.org/10.1002/adma.201101790>. Wang, Y., Gray, D., Berry, D., *et al.*, 2011. An extremely low equivalent magnetic noise magnetoelectric sensor. *Adv. Mater.* 23, 4111–4114. <https://doi.org/10.1002/adma.201100773>. Kambale, R.C., Patil, D., Ryu, J., *et al.*, 2013. Colossal magnetoelectric response of PZT thick films on Ni substrates with a conductive LaNiO₃ electrode. *J. Phys. D Appl. Phys.* 46, 092002. <https://doi.org/10.1088/0022-3727/46/9/092002>. 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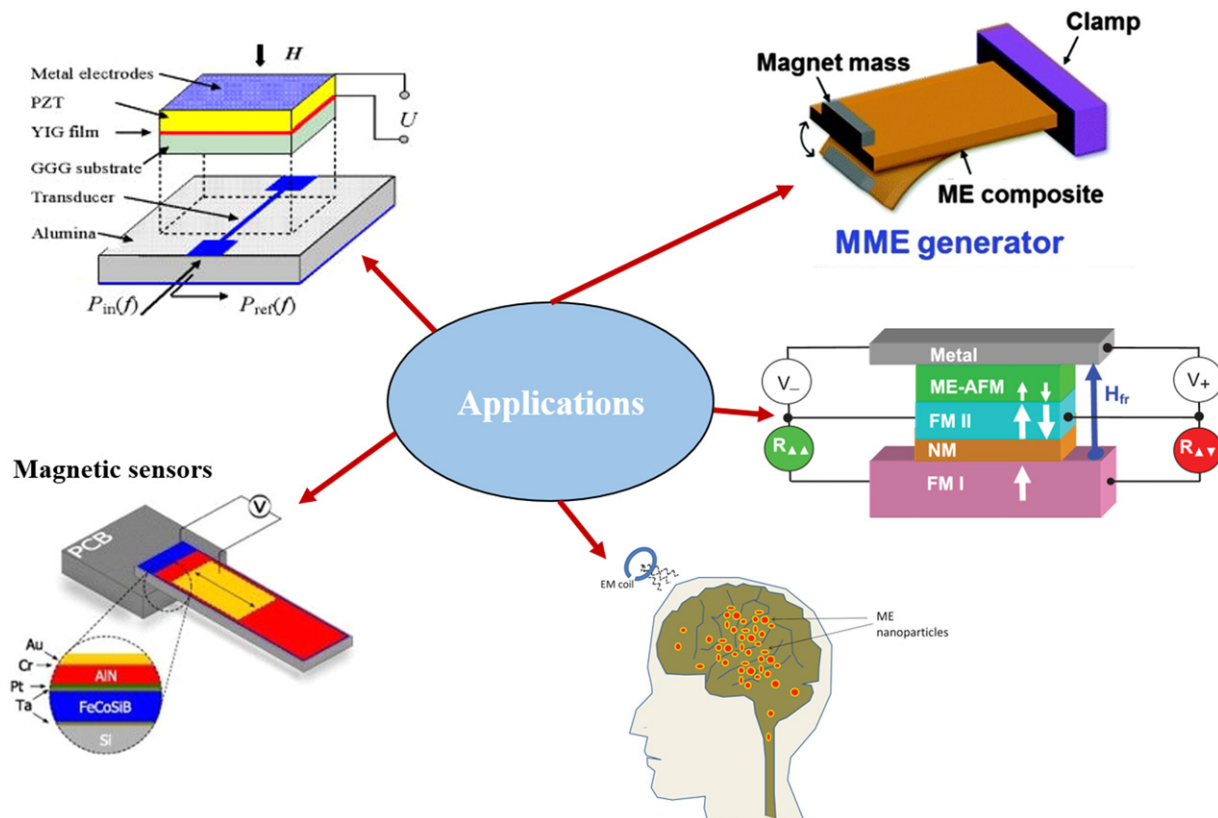


Fig. 16 Schematic representation of the vast applications of magnetoelectric (ME) composite thick and thin films.

films showed a relatively good saturation polarization of $75 \mu\text{C}/\text{cm}^2$ and a magnetization of 59 emu/g . A relatively high ME voltage coefficient of $94.5 \text{ V}/\text{cm}\cdot\text{Oe}$ indicates the potential application of these films in energy harvesting applications. Recently, Duan *et al.* reported ME coupling in $\text{LSMO}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{CFO}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ multilayer thin films fabricated on Si substrates with LMO as the bottom electrode using the chemical solution deposition method (Duan *et al.*, 2020). They achieved a relatively large ME voltage coefficient ranging from 20 to $50 \text{ V}/\text{cm}\cdot\text{Oe}$ without the presence of a DC magnetic field. In addition, different multilayer nanocomposite thin films such as PZT/NZFO , CFO/PZT , NFO/BTO , LCMO/BTO , PZT/LSMO , and $\text{Fe}_3\text{O}_4/\text{BTO}$ have been reported over the years. Although 2–2 nanocomposite thin films are easy to fabricate, their ME values are limited owing to the substrate clamping effect. To reduce the substrate clamping effect, Palneedi *et al.* fabricated flexible high-performance ME thin-film composites by depositing PZT on $\text{LaNiO}_3/\text{HfO}_2$ buffered Ni foil (Fig. 13(a) and (b)) (Palneedi *et al.*, 2017b). They obtained a relatively large ME voltage coefficient of $3.2 \text{ V}/\text{cm}\cdot\text{Oe}$ at off-resonance owing to the reduced substrate clamping effect and strong interfacial coupling (Fig. 13(c) and (d)). However, in 2010, Greve *et al.* reported the highest value for ME thin-film composites (Greve *et al.*, 2010a). They fabricated thin film ME composites consisting of a Si cantilever coated with AlN and Metglas using magnetron sputtering. They obtained ME voltage coefficients of $3.1 \text{ V}/\text{cm}\cdot\text{Oe}$ and $737 \text{ V}/\text{cm}\cdot\text{Oe}$ at off-resonance and resonance, respectively, upon magnetic field annealing of the films (Fig. 14(a) and (b)). The values obtained were the highest reported ME voltage coefficients for thin-film composites. In Fig. 15, we summarized most of the significant ME voltage coefficient values for various bulk and thick/thin film ME composites.

Applications

ME thin films have a large area of applications in novel and modern multifunctional devices, such as non-volatile memories, biomagnetic sensors, magnetic field sensors, power converters, energy harvesters, magnetometers mechanical antennas, and MEMS (Fig. 16). The coexistence of magnetization and electrical polarization makes them an excellent choice for multistate memory devices, such as magnetoelectric random-access memories (MERAM), which comprise the simultaneous effect of ferroelectric random-access memories (FeRAM) and magnetic random-access memories (MRAM) (Ma *et al.*, 2011). Conventional MRAMs use a magnetic field to write data by switching the magnetic dipoles. However, MRAMs require a high magnetic coercive field to write and a mechanical head to read the data, making them more power consuming and slower. Magnetic thin films grown on a ferroelectric layer are considered a promising solution to these issues. The magnetic coercive field of the ME structure can be

significantly reduced by applying an external electric field. Therefore, a smaller magnetic field is required to reverse the magnetization of the device, which decreases its power requirement.

Additionally, the coexistence of ferroelectric and magnetic polarization allows electric field-assisted four-state memory realization in a single device (Ma *et al.*, 2011). ME coupling of ME composites exhibits significant potential for electrostatically tunable microwave magnetic devices, such as filters, phase shifters, and resonators. Liu *et al.* demonstrated electric field-driven magnetization tunability in $\text{Fe}_3\text{O}_4/\text{PMN-PT}$ and $\text{Fe}_3\text{O}_4/\text{PZN-PT}$ composite thin films (Liu *et al.*, 2009). Similar to the converse ME (CME) effect, the direct ME (DME) effect, has a promising application as an AC and DC magnetic field sensor (Nan *et al.*, 2008; Zhai *et al.*, 2008). A high DME coupling coefficient is considered the most important criterion for the detection of weak DC and AC magnetic fields at resonance (Chu *et al.*, 2018). The ME voltage and sensitivity of ME composites are substantially enhanced by 1–2 orders of magnitude at resonance; therefore, an ME composite with a tunable resonant frequency is required for many applications. For example, ME composites have been widely employed to harvest magnetic fields and convert them into electrical potentials (Peddigari *et al.*, 2018; Annapureddy *et al.*, 2016, 2017). Similarly, ME composite thin films operated at its resonance frequency can be used in deep brain stimulation (DBS) medical treatment for patients suffering from tremors or dystonia. In this treatment, an array of electrodes is implanted deep into the patient's brain and stimulated at a well-defined frequency between 130 and 170 Hz. The simulated electrode area can be precisely located by tuning the mechanical resonant frequency of the ME sensor with that of the simulated frequency (Curtis *et al.*, 2020).

Apart from ME composite thin films, ME nanoparticles have been widely studied for their application as biological macromolecules for drug delivery purposes. Kargol *et al.* proposed an interesting idea of remotely controlling ion channel gating via externally applied magnetic field (Kargol *et al.*, 2012). In this approach, the magnetic field applied to ME nanoparticles generates an electric field in the vicinity of the cells, which can be locally modified for appropriate changes in the ion channel. Therefore, individual cells or targeted groups of cells can be targeted for drug delivery.

Conclusions

The present article reviews recent progress in the field of ME composites in bulk and thick/thin film forms. The interface strain plays an important role in the coupling between the magnetic and ferroelectric properties of ME composites via the magnetostriiction and piezoelectric response of the two phases. Nanocomposites have been commonly grown using the PLD method; however, recent work has demonstrated different robust scalable routes for large-scale fabrication of ME nanocomposites. In Fig. 15, we summarized most of the significant ME voltage coefficient values for various bulk and thick/thin film ME composites. In bulk composites, the laminated composites exhibited the largest ME voltage coefficient of 50 V/cm•Oe for Metglas/PMNPT laminates at off-resonance. The ME coefficient values for the ME nanocomposite thin films were below 1 V/cm•Oe and reached a few V/cm•Oe under resonance conditions. Among the ME nanocomposites, the 2–2 type nanocomposite films are easy to fabricate. Leakage current, which is a serious issue in 0–3 or 1–3 type nanocomposites, is also easy to mitigate in 2–2 type nanocomposite due to the insulating nature of ferroelectric layers. On the contrary, 1–3 type nanocomposites mitigate substrate clamping effect, which is generally observed in 2–2 type nanocomposites. Although ME nanocomposite thin films possess comparatively weaker ME coupling than bulk composites, they have potential application in miniaturized ME devices, such as integrated electronics, spintronic based memory devices, and medical devices.

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Metal Oxide Ceramic Gas Sensors

Sachin T Navale¹ and **Sanjit Manohar Majhi**, The Research Institute of Industrial Science and Division of Materials Science and Engineering Hanyang University, Seoul, Republic of Korea and Department of Materials Science and Engineering, Inha University, Incheon, Republic of Korea

Ali Mirzaei, Department of Materials Science and Engineering, Shiraz University of Technology, Shiraz, Iran

Hyoun Woo Kim, The Research Institute of Industrial Science and Division of Materials Science and Engineering Hanyang University, Seoul, Republic of Korea

Sang Sub Kim, Department of Materials Science and Engineering, Inha University, Incheon, Republic of Korea

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Abstract

Generally, ceramics are solid materials consisting of inorganic metal/metalloid/non-metal compounds with covalent/ionic bonds. Ceramics contain oxides, nitrides, and carbides and have considerable potential in different fields, including electronics, energy, chemistry, industry, and many more. In particular, the use of ceramic materials, especially metal oxides, as sensing elements to detect selectively detect toxic gases and volatile organic compounds (VOCs) has vastly increased in recent years. Particularly, semiconducting metal oxides (SMOs) based chemiresistive sensors are among the most popular for detecting various toxic gases and VOCs because of their high response, high stability, fast dynamics, and low costs. Typically, a chemiresistor is a material whose electrical resistance changes due to changes in the surrounding chemical environment. This review describes the fundamentals of SMOs-based chemiresistive sensors, the main characteristics of toxic gases and VOCs, and their gas detection mechanisms. In addition, the major challenges and the future significance of chemiresistive sensors are also outlined.

Key Points

- Importance of the sensing of toxic gases and vapors such as NO₂, CO, H₂S, CH₄.
- Introduction to ceramic gas sensors.
- Explanation of general sensing mechanism of metal oxide gas sensors.
- Role of noble metals on the gas sensing performance of ceramic gas sensors.
- Role of p-n heterojunctions on the gas sensing performance of ceramic gas sensors.

Introduction

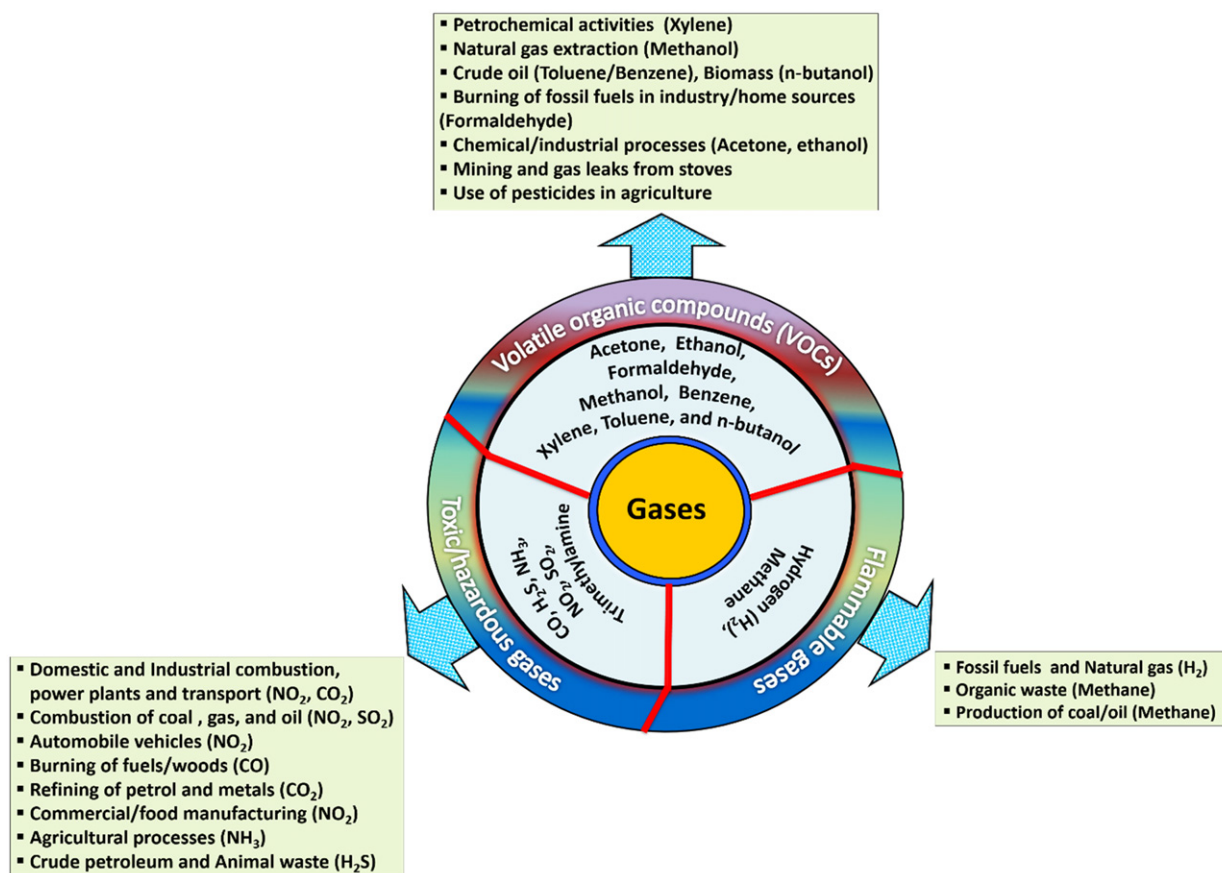
The life is impossible without gases. However, some gases such as NO₂ and CO are highly toxic and dangerous for human being. Also, some gases are flammable and explosive such as CH₄ and H₂. Greenhouse gases such as CO₂ are another category of gases. Therefore, there is a need for accurate detection of such gases. Even though human olfactory system is highly complex and can discriminate different gases and vapors, it fail to detect odorless gases or when the gas concentration is low. Hence, highly sensitive devices are necessary to detect gases and vapors. Gas sensors are devices that can detect a gas and response to it by an electronic signal. Different types of gas sensors are available and among them ceramic gas sensors using metal oxides are among the most popular gas sensors due to their high sensitivity, high stability, fast response and recovery times and cheap prices. In this chapter, we discuss ceramic gas sensors. First, we explain nature, toxic effect and flammability of dangerous gases. Then, chemiresistive gas sensors based on ceramic materials are introduced. We describe the history, design and materials used for realization of ceramic gas sensors. Afterwards, gas sensing performance parameters and affecting factors are discussed in detail. Finally, general sensing mechanism of gas sensing by this types of gas sensors are explained.

Toxic Gases and Vapors

Air pollution and climate change are two major challenges people face worldwide (Kinney, 2018). The most common cause of air pollution is the presence of ozone (O₃), SO₂, NO₂, CO, and particulate matter (Jung *et al.*, 2018). In particular, more than 90% of people are located in areas where air quality is poor and are exposed daily to air pollution hazards (Brugha *et al.*, 2018). Approximately 12% of all deaths in 2019 could be attributed to outdoor and indoor air pollution (Murray *et al.*, 2020). In India, for example, ~1.67 million deaths in 2019 were attributed to air pollution, approximately 17.8% of all deaths in the nation (Dandona *et al.*, 2019). Overall, air pollution is the 4th most crucial mortality risk factor and is more detrimental to health than obesity, high LDL cholesterol, and alcohol (Brauer *et al.*, 2021).

Toxic gases and VOCs that damage and threaten the environment and human beings are emitted into the atmosphere due to burning fossil fuels from different sources such as industries, cars, and even homes (Bao *et al.*, 2018; Wang *et al.*, 2018; Dong *et al.*,

¹Equal contribution.



Scheme 1 Schematic of different VOC types, toxic and flammable gases, and their sources.

2019). Even at low concentrations, exposure to toxic gases and vapors is hazardous for human health. Therefore, health- and safety-related agencies have established guidelines on the exposure limits of these poisonous gases (The National Institute for Occupational Safety and Health (NIOSH); Immediately Dangerous to Life or Health (IDLH); Documentation of the Threshold Limit Values and Biological Exposure Indices). The following briefly explains the main features of toxic gases and vapors.

- (i) **NO₂**: NO₂ with a three ppm of threshold limit value (TLV) (Wetchakun *et al.*, 2011), is a highly toxic and oxidizing gas that is released due to combustion processes such as fossil fuels in industries and cars (Kim *et al.*, 2020a). Exposure to NO₂ leads to lung irritation and decreases the absorption of oxygen molecules in red blood corpuscles. Besides, it causes acid rain (Mirzaei *et al.*, 2016a). At concentrations higher than 10 ppm, it can significantly damage the respiratory tract, causing emphysema, asthma, and chronic bronchitis (Bai *et al.*, 2021).
- (ii) **H₂S**: H₂S is a very toxic and flammable gas. It is usually found in basements, manholes, and sewer lines. At concentrations greater than 100 ppm, H₂S gas rapidly paralyzes the olfactory nerves. The main symptoms of H₂S exposure are asphyxia, which can result in suffocation. Inhaling high levels of H₂S (more than 1000 ppm) paralyzes the respiratory nerve center, which can cause suffocation and sudden physical collapse (Mirzaei *et al.*, 2018a). Thus, it is important to monitor the levels of H₂S in the petrochemical and coal industries (Gong *et al.*, 2006). H₂S is also a biomarker, and the presence of high concentrations of H₂S (> 250 ppb) in exhaled breath indicates periodontal disease (Kaur *et al.*, 2017).
- (iii) **CO**: It is an odorless, colorless, and tasteless gas that kills people silently. It is emitted during the incomplete combustion of fuels (Van Tong *et al.*, 2021). The TLV of CO is 25 ppm (Ani *et al.*, 2020). However, even inhalation of CO (> 15 ppm) is dangerous to humans. At high concentrations, it is hazardous gas. Exposure to 0.5% CO for 10 min will likely result in immediate death. More than 15,000 cases of intentional CO poisoning occur each year (Kim *et al.*, 2020b). Moreover, CO is also a biomarker, and the concentration of CO in exhaled breath (EB) of patients is higher than the CO concentration in the EB of ordinary people (Vaks *et al.*, 2014).
- (iv) **NH₃**: NH₃ is among the most commonly used chemicals in different industries. It is primarily emitted from chemical plants and is found in the exhaust of motor vehicles (Seekaew *et al.*, 2019). The TLV of the NH₃ gas is set to 25 ppm (Tian *et al.*, 2017). The inhalation of NH₃ (exceeding the safe limit) can result in life-threatening illnesses as it is toxic and corrodes the skin and lungs (Ismail *et al.*, 2020).

Table 1 Properties of different VOCs and toxic gases.

<i>Gas name</i>	<i>IDLH</i>	<i>TLV</i>	<i>Health issues in humans</i>	<i>Properties</i>	<i>References</i>
C ₃ H ₆ O	2500 ppm	750 ppm	It causes muscle weakness, dry mouth, fatigue, dizziness, nausea, and narcosis and is harmful to the nervous system.	Colorless liquid. Used as a solvent, used to develop pharmaceuticals. Emits a pungent odor. Used to dissolve plastic and used in laboratories as a reagent.	(Patnaik, 2007)
HCHO	20 ppm (OSHA)	0.1–0.3 ppm	Human carcinogen (pulmonary damage and leukemia at 6 ppm)	Colorless and flammable.	(Zhu and Wu, 2015; Castro-Hurtado <i>et al.</i> , 2013)
C ₂ H ₅ OH	3300 ppm (NIOSH)	(1000 ppm -STEL) (ACGIH)	Breathing difficulty, eye irritation, drowsiness, and headache	Volatile, Colorless, and inflammable.	(Kadir <i>et al.</i> , 2014)
NO ₂	13 ppm (NIOSH)	0.3 ppm (ACGIH)	Causes lung damage. Irritates the eyes and produces ozone	Emits pungent odor. Not flammable.	(Lee <i>et al.</i> , 2018; Schwela, 2000)
H ₂ S	100 ppm (NIOSH)	1–5 ppm (ACGIH)	Highly reactive toward hemoglobin. Causes fatal damage to the olfactory system	Emits rotten egg smell. Colorless and toxic.	(Annanouch <i>et al.</i> , 2015; Tian <i>et al.</i> , 2017b; Yang <i>et al.</i> , 2017)
NH ₃	300 ppm (NIOSH)	25 ppm (ACGIH)	Harmful to skin/eyes/ respiratory tract of humans. Corrosive and an irritant	Colorless, corrosive, and hazardous.	(Timmer <i>et al.</i> , 2005)
Cl ₂	10 ppm (NIOSH)	0.1–0.4 ppm (ACGIH)	Causes eye irritation (>5 ppm)	Characterized by an irritating odor. Harmful, quickly reacts with water to form corrosive acid. presence in ozone layer, fatal to human being.	(White and Martin, 2010)
Acetic acid	50 ppm (NIOSH)	10–15 ppm (ACGIH)	Causes Eyes/nose/throat irritation, cough, chest tightness, fever, confusion, and headache	Colorless and emits vinegar-like smell. It is flammable.	(Bhamore <i>et al.</i> , 2016)
CO	1200 ppm (NIOSH)	50 ppm (OSHA) and 35 ppm (NIOSH)	Causes headache, loss of consciousness, fatal death (attributable to the binding with hemoglobin), reduced oxygen transportation, dizziness, collapse, and nausea	Colorless, odorless, tasteless, and non-irritating.	(Hjiri <i>et al.</i> , 2014; The National Institute for Occupational Safety and Health NIOSH, 2015)
Trimethylamine	—	15 ppm -STEL (OSHA)	Causes throat, nose, skin, and eye irritation	Causes blurred vision and cough. Irritates the eyes/skin/ nose/throat, respiratory system.	(Chen <i>et al.</i> , 2014; Documentation of the Threshold Limit Values and Biological Exposure Indices
H ₂	N/A	N/A	Causes stinging of the nose/throat and vomiting. Asphyxiant gas that result in dizziness/ headaches/drowsiness/nausea	Highly flammable, colorless, and tasteless. Used for metal smelting. Characterized by low ignition energy (0.017 mJ). Highly explosive. Used as fuel in petroleum extraction and glassmaking.	(Wang <i>et al.</i> , 2013)

OSHA: Occupational Safety and Health Administration, NIOSH: National Institute for Occupational Safety & Health, ACGIH: American Conference of Governmental Industrial Hygienists, N/A: Not Available, STEL: Short-term Exposure Limit.

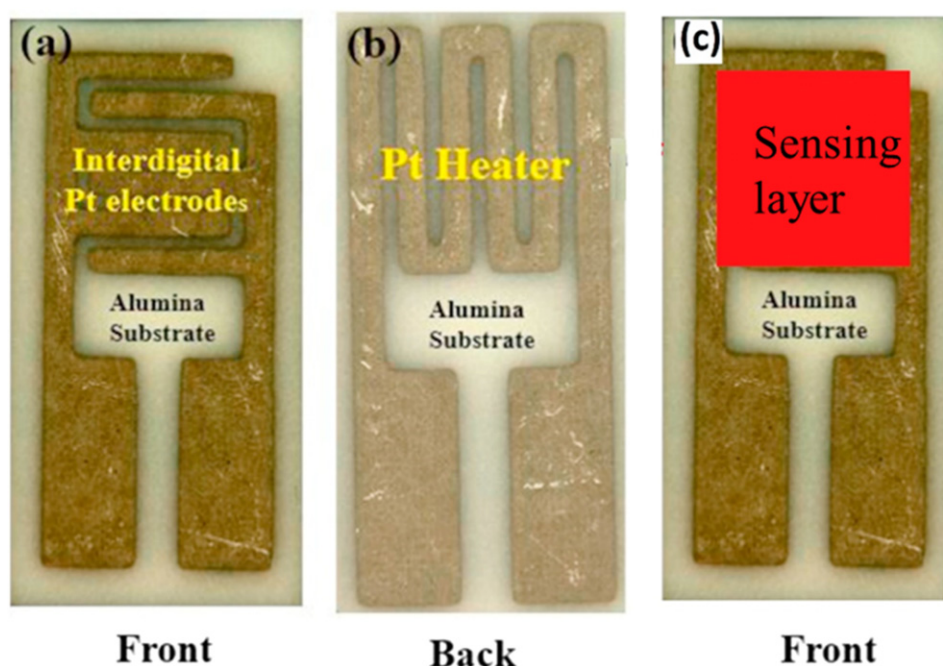


Fig. 1 A photograph of the typical structure of a gas sensor (a) front side (b) backside. (c) after deposition of the sensing layer. Reproduced from ref. Mirzaei, K. Janghorban, B. Hashemi, M. Bonyani, S.G. Leonardi, G. Neri, (2016b). A novel gas sensor based on Ag/Fe₂O₃ core-shell nanocomposites. *Ceramics International* 42(16), 18974–18982. <https://doi.org/10.1016/j.ceramint.2016.09.052>, with the permission of Elsevier.

- (v) **SO₂**: SO₂ is a toxic and corrosive gas that is emitted into the atmosphere during numerous industrial processes. It is also emitted during various natural phenomena (Kwak *et al.*, 2019; Zhou *et al.*, 2019). The TLV of SO₂ was set to 5 ppm (Salih and Ayesh, 2021). It can be transformed into sulfuric acid, found in acid rain. Acid rain has the potential to reduce agricultural productivity, affect flora/fauna, and damage the whole plant ecosystem (Gaiardo *et al.*, 2020). Exposure to high levels of SO₂ gas can cause cardiovascular diseases, respiratory illnesses, and breathing problems in humans (Thangamani and Pasha, 2021).
- (vi) **CH₄**: CH₄ is a flammable, colorless/odorless gas that is explosive at high levels (5–15%). It is a key component of natural gas and mainly serves as a fuel for the production of heat and light (Lee *et al.*, 2011). Furthermore, it is a strong greenhouse gas, almost 25 times more powerful than CO₂ (Bunpang *et al.*, 2019). CH₄ explosions and CO poisoning occur during coal mining. These are the two common gas-based disasters (Lassey, 2007).
- (vii) **CO₂**: CO₂ is a typical greenhouse gas emitted from automobiles, industries, and electric power generators (Wang *et al.*, 2021). Thanks to its excellent physicochemical features (inert and water-soluble features, high density), CO₂ is broadly utilized in the food industry. It is also used as a fire extinguisher and for developing lasers and refrigerants (Thomas *et al.*, 2021). Adsorption of the short wavelengths reflected from the earth to space causes the earth's temperature to rise. This causes droughts and floods. This also accelerates the ice melting rate at the poles (Lin and Fan, 2020). During the process of greenhouse planting, low CO₂ levels (<300 ppm) have to be detected, and through the modified atmosphere packaging process of fruits/vegetables, high CO₂ levels (≈25%) should be monitored (Molina *et al.*, 2020).
- (viii) **VOCs**: Generally, VOCs are identified as high vapor pressure and low boiling point organic chemicals. These are volatile substances (Kawamura *et al.*, 2006; Cao *et al.*, 2014). The most important VOC pollutants are *n*-butanol (C₄H₁₀O), xylene (C₈H₁₀), acetone (C₃H₆O), toluene (C₇H₈), ethanol (C₂H₅OH), benzene (C₆H₆), methanol (CH₃OH), and formaldehyde (HCHO). **Scheme 1** presents the different types of VOCs, toxic gases, and flammable gases and their sources.

In addition, the physical properties, uses, exposure limits, and human health effects of various toxic gases and VOCs are present in **Table 1** (Annanouch *et al.*, 2015; Bhamore *et al.*, 2016; Castro-Hurtado *et al.*, 2013; Chen *et al.*, 2014; Hjiri *et al.*, 2014; Kadir *et al.*, 2014; Lee *et al.*, 2018; Patnaik, 2007; Schwela, 2000; Tian *et al.*, 2017b; Timmer *et al.*, 2005; Wang *et al.*, 2013; Yang *et al.*, 2017; Zhu and Wu, 2015; White and Martin, 2010; Documentation of the Threshold Limit Values and Biological Exposure Indices; The National Institute for Occupational Safety and Health NIOSH, 2015).

Chemiresistive Gas Sensors

Gas sensors are required in various areas, particularly in industries, automobile manufacturing units, and mines for environmental monitoring (indoor and outdoor) (Mustafa and Andreescu, 2018; Korotcenkov and Cho, 2017). Furthermore, they are necessary to recognize hazardous gases and vapors in homes and public places. Chemiresistive gas sensors based on SMOs have unique

features such as cost-effectiveness, miniature form, and robustness. Furthermore, they are easy to fabricate and have high stability, high sensitivity, and fast dynamics. These features make them often as the first choice of gas sensors in different areas (Mirzaei *et al.*, 2018b; Mirzaei and Neri, 2016). The idea of exploiting metal oxides as an active gas sensing materials goes back to 1954, wherein Heiland used ZnO as a gas detection element, i.e., the extension of Brattain and Bartein's idea which reported that the variation in surrounding atmosphere can change electrical properties of Ge. Later, driven by gas explosions in Japan, Seiyama (1962) developed a simple resistive gas sensor based on ZnO thin films to detect propane that gave nearly 100 times higher response than the thermal conductivity detector used at that time. A few years later, in 1968, Taguchi marketed a simple TiO₂ gas sensor to detect low levels of combustible/reducing gases (Navale *et al.*, 2022). Gas sensors based on MOS often are prepared in thin-or thick films on flat or tubular insulating substrates. As shown in Fig. 1, a typical SMOs-based gas sensor contains three components: (i) the sensing layer (to recognize the target gas), which is a MOS material, (ii) contact electrodes, e.g., Au, and Ag-Pd (to detect changes in resistance), and (iii) a heating element such as Pt (for controlling sensor temperature) (Mirzaei *et al.*, 2016).

In chemiresistive sensors, the electrical resistance of sensing materials changes when target gases are present. Depending on the type of sensing layer and oxidizing or reducing nature of the gas, an electrical signal appears that shows the existence of a particular gas in the environment. Therefore, the effectiveness of the chemiresistors depends mainly on the direct chemical interactions between the sensing material and the target gas. Most of the SMOs-based gas sensors (> 90%) are *n*-type (Kim and Lee, 2014). This could be attributed to the fact that the *n*-type SMOs-based sensor generally exhibits higher sensitivity due to more charge carriers and higher mobility of charge carriers compared to its counterpart (i.e., *p*-type SMOs-based sensor) (Sahin *et al.*, 2014). For example, In₂O₃ with a band gap of 3.5 eV, stands out as an excellent chemiresistive sensor material due to excellent electrical conductivity and high mobility (160 cm²•V/sec) (Pawar *et al.*, 2019). Thanks to their unique features, MOS also can be used in different areas such as energy storage (Zhao *et al.*, 2018), catalysts (Tsoukalou *et al.*, 2019), microelectronics (Zhu *et al.*, 2019), and solar cells (Chen *et al.*, 2018) to name a few of them.

Gas Sensing Performance Parameters and Affecting Factors

The efficiencies of chemiresistive SMOs-based gas sensors are described using the concept of "3S" (sensitivity, selectivity, and stability) (Lin *et al.*, 2017; Yuan *et al.*, 2019). Ideally, a gas sensor should be susceptible to a particular gas. It should work efficiently under conditions of low temperature and exhibit long-term response stability. The main factors that control the performance of a chemiresistive sensor are response, the response time (τ_{res}), recovery time (τ_{rec}), selectivity, repeatability, the limit of detection (LOD), and long-term response stability (Choi and Jang, 2010). The response is defined as a change in the resistance due to a change in the target gas concentration. The term τ_{res} represents a 90% variation in the sensor's resistance in the presence of the target gas. A 90% recovery of the sensor resistance after removing a target gas is represented by τ_{rec} (Mirzaei *et al.*, 2019). In addition, selectivity is an important factor determining the effectiveness of the chemiresistive sensors. As a gas detecting device is sensitive to interfering gases, cross-sensitivity is observed, which often leads to a false alarm. Selectivity is described as the capability of the device to identify a definite gas in the presence of other interfering gases (Gurlo *et al.*, 2006). Instead, the repeatability of a chemiresistive sensor is the ability of a sensor to deliver reproducible behavior when repeated measurements are performed under similar measurement conditions. The LOD is defined as the capacity of a sensor to sense the lowest possible concentration of the gas at a given working temperature (Umar and Hahn, 2010). Finally, the stability of a sensor is described as having the same sensing behavior over a long time, for example, after three months (Baharuddin *et al.*, 2019).

Recently, small and compact gas sensors, which are portable and can be easily integrated into smartphones, have been developed (Burgues and Marco, 2018). However, most of the gas sensors have low selectivity in pristine form and high temperature operation that leads to high energy consumption. Moreover, SMOs-based gas sensors cannot function effectively under highly humid conditions. As a result, researchers have focused on improving sensor sensitivity through various strategies. Various parameters, such as surface morphology, microstructure, surface area, porosity, structure of the nanocomposites, presence of the defects and working temperature, have a remarkable impact on the effectiveness and characteristics of SMOs-based sensors (Comini *et al.*, 2009; Lee, 2009; Tiemann, 2007; Zhang *et al.*, 2016). Numerous strategies have been used to synthesize SMOs-based gas sensors with various surface morphologies and heterojunctions (Gu *et al.*, 2018; Wang *et al.*, 2019; Sun *et al.*, 2017; Wei *et al.*, 2018).

Gas Sensing Mechanism

The electrical resistance of *n*-type SMOs-based gas sensors decreases when it is exposed to reducing gases, e.g., NH₃, H₂, H₂S, and CO. However, the electrical resistance increases when they interact with oxidizing gases, e.g., NO₂, SO₂, and ozone (O₃). In contrast, the opposite effect is actual for *p*-type SMOs-based gas sensors (Baharuddin *et al.*, 2019; Miller *et al.*, 2014; Xu and HO, 2017). Basically, the response value of SMOs-based gas sensors is remarkably influenced by the nature and extent of interactions amongst the detection layer, adsorbed oxygen, and the target gas (Walker *et al.*, 2019). The target gases are either physisorbed or chemisorbed on the sensors' surface. During physisorption, the target gas molecules are adsorbed at low working temperatures. However, chemisorption involves in-charge transfers attributable to the bond configurations of the adsorbed gas. It also depends on the nature of the atoms present on the sensor surface (Walker *et al.*, 2019). In general, when an *n*-type SMOs sensor is exposed to air, the oxygen molecules of the air get adsorbed on the material's surface. This causes the electrons to be removed from the

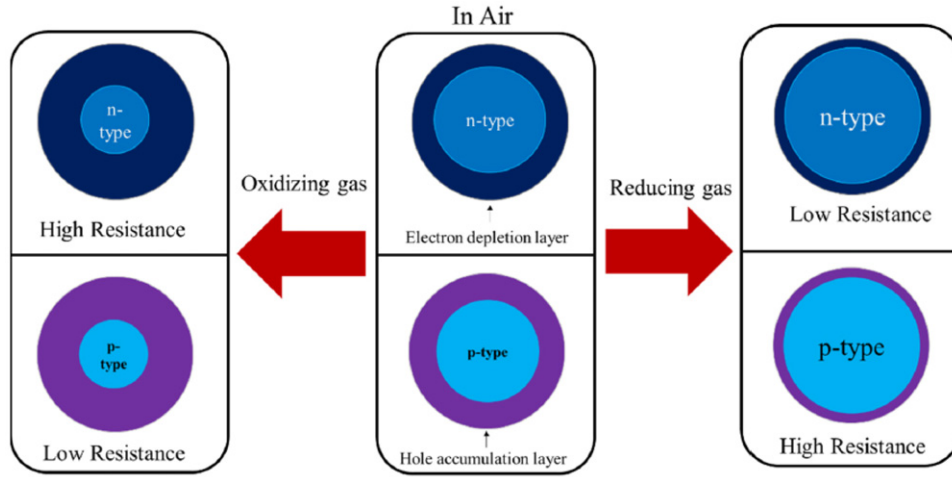


Fig. 2. Mechanism of gas sensing for *n*- and *p*-type SMOs-based chemiresistive gas sensors.

conduction band (CB) of the SMO material and thereby enhancing the concentration of negatively charged oxygen ions, such as O^{2-} , O_2^- , and O^- , on the surface of sensor. The generation of these chemisorbed oxygen species depends mainly on the sensor's operating temperature (Ren *et al.*, 2020). When sensing devices function at low working temperatures (~ 25 – 150°C), the process of adsorption of oxygen molecules can be designated by the following equation:



At higher working temperatures, the O_2^- molecules dissociate into singly/doubly charged oxygen ions following the abstraction of electron(s) from the CB of the SMO material:



Consequently, an electron depletion layer is created on the sensor surface, and this can be attributed to the lower amounts of electrons (due to adsorption by oxygen species) in this layer relative to core parts. Under these conditions, the sensor resistance increases in air. The resistance subsequently decreases when the sensor interacts with reducing gases such as CH_4 (Fig. 2). On the other hand, for *p*-type sensors, due to abstraction of electrons a hole accumulation layer (HAL) is formed on exposed surface of the sensor, resulting in decrease of resistance relative to air. When exposed to target gases like CO, the HAL thickness decreases, resulting in increased sensor resistance, as depicted in Fig. 2. A depletion layer at the surface causes band bending. The interconnection of polycrystalline materials hinders the electron flow of one grain to the other with grain boundaries. This causes the generation of a potential barrier (V) at the surface, which increases the sensor's electrical resistance.

A potential barrier height significantly depends on the amount of adsorbed oxygen molecules (Sze and Ng, 2006). The dynamic interactions between the target gas and chemisorbed oxygen species cause a change in the carrier concentration and the potential barrier height (Fig. 3) (Abideen *et al.*, 2015).

In the presence of a reducing gas, a change in the sensor resistance and the reduction in the potential barrier height occurs because of the release of electrons at the sensor surface (Ren *et al.*, 2020; Dey, 2018):



Here, X, X', and n denote the target gas, product gas, and the number of released electrons, respectively.

The sensing potential of the sensor is primarily controlled by three factors, i.e., the receptor function, the transducer function, and the utility factor (Yamazoe, 2005). The primary role of the receptor of the gas sensor is to recognize the oxygen species and the target gas in the surrounding environment. The sensing layer helps to achieve this end. The extent of gas molecules adsorption depends significantly on the surface area of the detection materials. The surface can be modified by tuning the shape, surface morphology, and size of the synthesized material. The transducer dictates the electronic changes occurring due to the interactions between the detection materials and the target gases (to a signal output) as a change in resistance. The utility factor enables the entry of the gaseous molecules through the pores of the detection materials, influencing the sensor response. The factors mentioned above can be studied to obtain practical guidelines for developing new materials with appropriate structures (Nasiri and Clarke, 2019).

The detection features of gas sensors can be improved by decorating their surfaces with noble metals like Au, Pt, Pd, Rh, and Ag. Typically, chemical sensitization and electronic sensitization mechanisms are accountable for improving gas detection properties when noble metals are present. Commonly, chemical sensitization is primarily demonstrated as a catalytic effect. In such sensitization, the target gas molecules dissociate into atoms at the surface of the noble metal and spill over onto the surface of the host

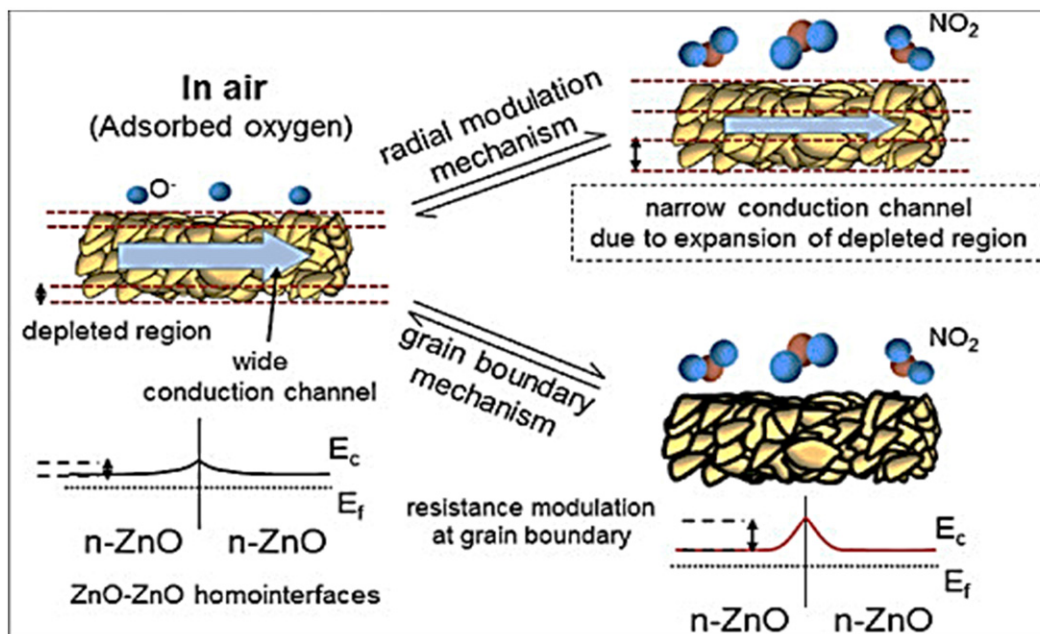


Fig. 3. Radial modulation and modulation of potential barriers for ZnO nanofiber gas sensor. Reproduced from ref. Abideen, Z.U., Katoch, A., Kim, J.-H., Kwon, Y.J., Kim, H.W., Kim, S.S., 2015. Excellent gas detection of ZnO nanofibers by loading with reduced graphene oxide nanosheets. *Sensors & Actuators, B: Chemical* 221, 1499–1507. <https://doi.org/10.1016/j.snb.2015.07.120>, with the permission of Elsevier.

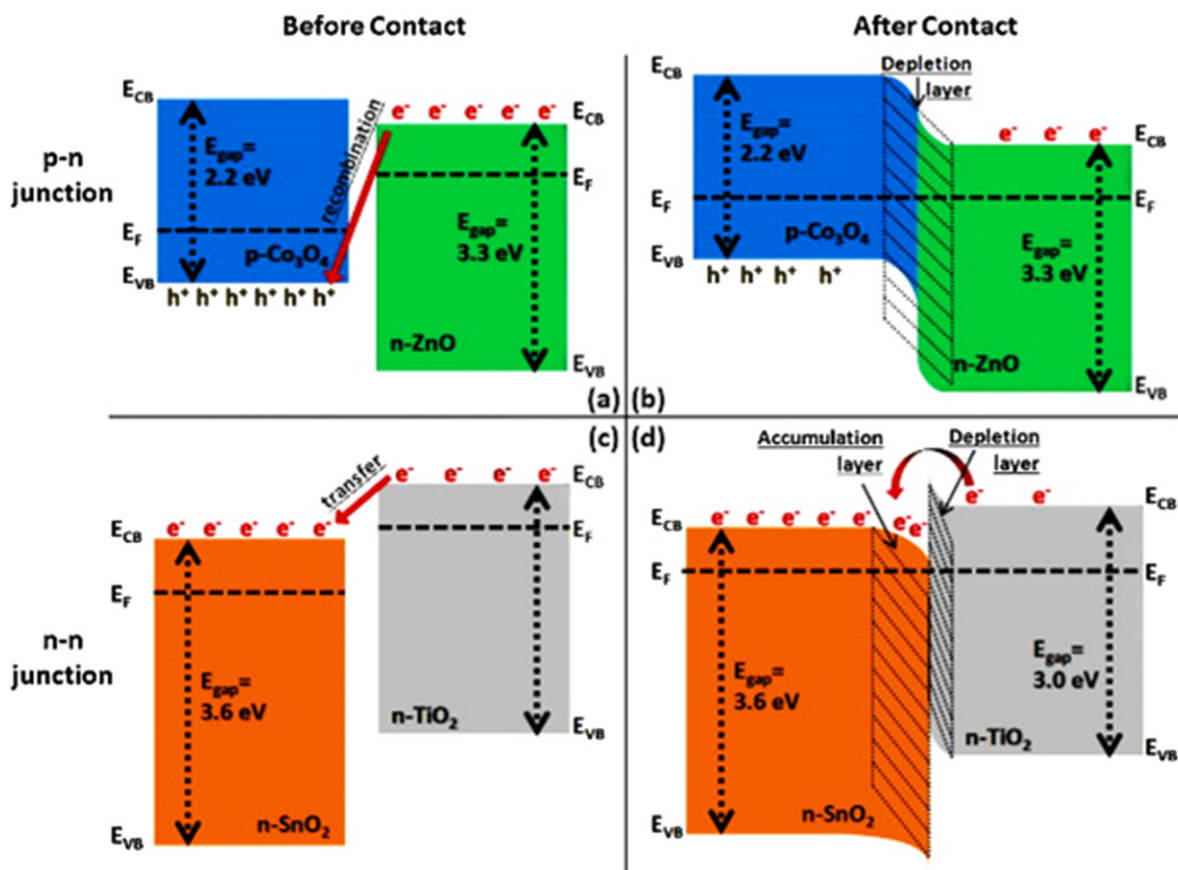


Fig. 4 (a)-(b) Formation of heterojunctions between p-Co₃O₄/n-ZnO. (c)-(d) Formation of heterojunctions between n-SnO₂/n-TiO₂. with the permission of Elsevier. Reproduced from ref. Miller, D.R., Akbar, S.A., Morris, P.R., 2014. Nanoscale metal oxide-based heterojunctions for gas sensing: a review. *Sensors and Actuators B: Chemical* 204, 250–272. <https://doi.org/10.1016/j.snb.2014.07.074>.

material, thereby speeding up gas detection reactions by a subsequent reaction with pre-adsorbed oxygen ions on the surface of the sensor. Instead, electronic sensitization involves a direct electronic interaction between the surface of SMOs and noble metals. As the oxidation state of noble metals changes with the surrounding atmosphere, the electronic state of SMOs changes accordingly. Principally, Ag and Pd are supposed to form stable oxides in the air, while they are simply reduced to metals with a reducing gas. The changes in work function indicate that each oxidized noble metal produces a highly electron-depleted layer within SMOs, whereas electronic interaction is inhibited when it is reduced to metal (Mirzaei *et al.*, 2020).

The use of *p-n*, *n-n*, and *p-p* heterojunctions is another efficient means of improving the performance of SMOs-based gas sensors. Due to having different values of work functions, when other MOS materials are in contact, the electrons flow from one material to another to equalize the Fermi levels. This causes the extension of the electron depletion layers in the air. When exposed to reducing or oxidizing gases, the thickness of the electron depletion layer in heterointerface changes, resulting in resistance modulation. Fig. 4(a)-(b) shows this mechanism for *p*-Co₃O₄/*n*-ZnO heterojunctions that cause band bending at heterojunction interfaces. A *p-n* junction may be developed between *p*-type Co₃O₄ and *n*-type ZnO. The existing low-energy valence band states (holes) instigate the transfer of electrons across the interface and the equilibration of Fermi energies (E_F). A depletion layer is developed on both sides of *p-n* junction because of the recombination, forming a potential barrier for electron flow. Fig. 4 (c)-(d) illustrates the formation of *n-n* junction between *n*-type SnO₂ and *n*-type TiO₂ (Miller *et al.*, 2014). A depletion layer formed at *n*-TiO₂ surface as a result of electron loss, and an accumulation layer formed at SnO₂ surface as a result of addition of the electrons, that improves the adsorption of oxygen. A potential barrier has also been created at the interface.

Conclusions and Future Outlooks

Over the past few years, research in chemiresistive gas sensors has developed rapidly. While significant advances have been made in the design of SMOs-based gas sensors, obtaining high detection performances doesn't remain easy. Although they could operate effectively under high operating temperatures, developing highly sensitive sensors that can work in ambient temperature conditions is essential to reduce energy consumption. In general, a combination of SMOs with carbon, and/or polymer materials could be used efficiently for developing low temperature sensors.

Developing reliable gas sensors for flexible devices is another problem with SMOs-based gas sensors. Efficient techniques have yet to be developed which can be used successfully to manufacture SMOs and integrate them with flexible substrates. Flexible and wearable sensors may serve as direct points of care for real-time recognition of analytes. Developing devices that can be used at room temperature can provide a platform for designing portable and flexible SMOs-based devices. Additionally, humidity negatively affects the response of SMOs-based gas sensors. As a result, continuous efforts should be made to develop robust sensors to achieve high sensor performance under various environmental conditions. The reasons for selectivity to a particular gas have rarely been revealed. Pattern recognition can be achieved in the presence of different sensing layers, which can be used for designing sensor arrays. A pattern recognition analysis methodology can be used to improve the sensitivity of the devices toward specific gases. This indicates that appropriate techniques or realistic models should be developed to understand the actual mechanism of gas detection further.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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Ferroelectric Ceramic-Polymer Nanocomposites for Applications in Dielectric Energy Storage Capacitors

Tarun Garg¹, Yadavindra Department of Sciences, Punjabi University Guru Kashi, Talwandi Sabo, Bathinda, Punjab, India
Navneet Dabra², Department of Sciences, Mata Sahib Kaur Girls College, Talwandi Sabo, Bathinda, Punjab, India
Jasbir S Hundal³, Punjabi University Guru Kashi, Talwandi Sabo, Bathinda, Punjab, India

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Abstract

Dielectric capacitors due to their ultrahigh power density capabilities are useful in pulsed power electronics. The operating voltage of dielectric capacitor depends on the intended application and, the concomitant enhancement in permittivity and electrical breakdown strength of dielectrics to improve their storage energy density properties would make them useful in wide range of applications. In this regard, the ferroelectric ceramic-polymer composites are the emerging class of dielectrics preserving enhanced dielectric properties of ceramic nanofillers and, high breakdown strength and flexibility of polymers. The polyvinylidene difluoride PVDF and barium calcium zirconium titanate BCZT composites are extensively explored due to excellent intrinsic ferroelectric properties of PVDF and BCZT leading to efficient energy storage in PVDF/BCZT composites. The main strategies to improve capacitive energy storage in polymer-nanocomposites include (i) tailoring shape and size of nanoceramics for enhanced electrical properties, (ii) surface-modifications on nanoceramics for better ceramic-polymer interfacial bonding, and (iii) novel synthesis techniques to feasible pathway for designing materials. This chapter includes the basics principle and importance energy storage capacitor and various parameters to evaluate capacitive energy storage in dielectrics. The development in dielectric materials and synthesis techniques dedicated to nanoparticles, polymers and polymer-nanocomposites appropriate to meet the requirements in energy storage application are discussed. Finally, the current approaches to achieve high-performance energy storage dielectrics are presented.

Dielectric Energy Storage Capacitors

Introduction

A capacitor is an electronic component which consists of two metallic plates being separated by a region of no conductivity. Either a vacuum or an electrically insulating material could act as a non-conductive region in a capacitor. A conventional dielectric capacitor generally consists of two electrodes with a thin layer of dielectric material in between them. Thin dielectric materials whose two opposite surfaces coated with conducting paste constitute a dielectric capacitor. Due to the different polarization phenomenon (electronic, ionic, polar/orientational and interfacial) involved in a dielectric medium under the influence of applied electric field, the induced electrical charge can be stored at the conducting surfaces of capacitor (Pirzada and Sabir, 2018).

The capacitance C of a capacitor is defined as rate of change of electric charge dQ to corresponding change in electric potential dV as expressed below:

$$C = \frac{dQ}{dV} \quad (1)$$

The SI (International System of Units) unit of capacitance is farad F . One farad capacitance means one coulomb of charge developed on the electrodes or metallic plates which have the potential difference of one volt.

Consider a parallel plate dielectric capacitor with opposite charge $\pm Q$ on two conductive plates of area A (Fig. 1). The thickness of dielectric material or the distance separating the two conducting plates is d . Then, the surface charge density will be $\sigma = \frac{\pm Q}{A}$.

According to Gauss's law, electric field inside the oppositely charged parallel plates with surface charge density σ , will have the magnitude of $E = \frac{\sigma}{\epsilon}$ where, ϵ is the permittivity of insulating dielectric medium between the plates.

The voltage V between the plates can be calculated as

$$V = \int_0^d E(y)dy = E(y) \int_0^d dy = E(y)d = \frac{\sigma}{\epsilon}d = \frac{Qd}{A\epsilon}$$

Using $Q = CV$ and, substituting for Q will give the expression for capacitance in terms of ϵ , A and d as

$$C = \frac{\epsilon A}{d} \quad (2)$$

Hence, the capacitance of a dielectric capacitor can be improved by following selections or modifications in the dielectric medium: Fig. 2

1. High permittivity: A dielectric medium with a large permittivity increase the capacitance. Permittivity measures the capability of any medium to store electric charge or electrical energy in an electric field.

¹ORCID ID: <http://www.orcid.org/0000-0003-3915-566X>.

²ORCID ID: <http://www.orcid.org/0000-0002-1706-0160>.

³ORCID ID: <http://www.orcid.org/0000-0002-6271-7950>.

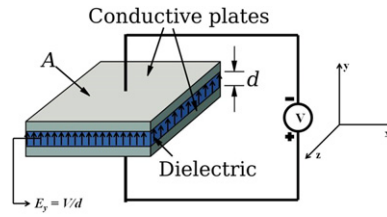


Fig. 1 Parallel plate capacitor consisting conductive plates of area A with dielectric medium of thickness d in between separating the plates.

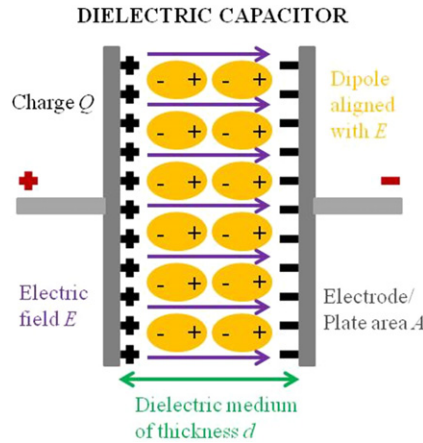


Fig. 2 The separation of charge in a parallel-plate capacitor generating an electric field inside the dielectric medium between the plates. Adapted from Ref. Hao, X., 2013. A review on the dielectric materials for high energy-storage application. *J. Adv. Dielectr.* 03, 1330001. (1–14). Also, permission to reprint from Ref. Palneedi, H., Peddigari, M., Hwang, G.-T., Jeong, D.-Y., Ryu, J., 2018. High-performance dielectric ceramic films for energy storage capacitors: Progress and outlook. *Adv. Funct. Mater.* 28, 1803665.(1–33).

2. High dielectric strength: Reducing the thickness d of dielectric medium will increase the capacitance. However, with thin dielectric medium, the distance between the conducting plates also decreases. The magnitude of electric field strength generated between the plates $E = \frac{V}{d}$ is inversely proportional to the distance between the plates. So, reducing the thickness d of dielectric medium will increase the value E . If the value of E exceeds the certain threshold value called dielectric breakdown strength E_{BD} of a dielectric material between the plates, the material will lose its insulating property. Basically an avalanche multiplication of electrons will happen after threshold value of electric field. A dielectric medium with high dielectric strength is preferable.
3. Large surface area: Increasing the surface area A of dielectric medium with electrodes will increase the capacitance.

If V is the voltage on capacitor at any instant then the amount of work done for the small increment in charge dQ is given by $dW = VdQ$. The work done to charge a capacitor is stored as electrical energy. The total work done in establishing an electric field in capacitor from its uncharged state can be expressed as

$$W = \int_0^Q V(Q)dQ = \int_0^Q \frac{Q}{C}dQ = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} VQ = \frac{1}{2} CV^2 \quad (3)$$

The total energy remains stored until capacitor discharges or charge is removed. So, a capacitor might be assumed as a type of rechargeable battery, storing charge and energy to use later. For an ideal capacitor the electrical energy is stored and released only without dissipating any part of it. However, due to the incapability to meet the ideal conditions the imperfect capacitive dielectric material create resistance and due to that all capacitors lose some part of stored energy. At any constant voltage V , the capability of a capacitor to store the amount of energy can be increased simply by improving the capacitance. The dielectric materials having large value of permittivity, possessing greater dielectric breakdown strength, and lesser losses are always desirable for their use in capacitors to store electrical energy.

Consider a RC-circuit having fully charged capacitor of capacitance $C = 100 \mu\text{F}$ in series with resistor having resistance $R = 1 \text{ k}\Omega$ (Fig. 3).

When a charged capacitor is connected to resistor, it will start discharging and there is a decay of charge and voltage drop along the capacitor. For a fully charged capacitor, the decaying of charge Q and voltage drop V across the capacitor at any time t can be expressed as an exponential function of t as given by equation below

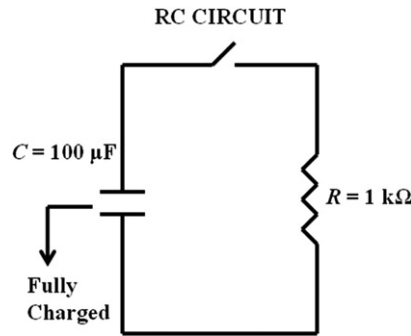


Fig. 3 A resistor-capacitor RC circuit demonstrating discharging of a capacitor.

$$\begin{aligned} V(t) &= V_c e^{-\frac{t}{\tau}} \\ Q(t) &= CV_c e^{-\frac{t}{\tau}} = Q_c e^{-\frac{t}{\tau}} \end{aligned} \quad (4)$$

where; V_c and Q_c are the voltage and charge across fully charged capacitor, and τ is the time constant for RC -circuit. $\tau = RC$, is the time taken by a fully charged capacitor to discharge exponentially to 37% of its original value. Approximately five times the τ -value is the time a fully charged capacitor takes to discharge completely. If $R = 1 \text{ k}\Omega$ and $C = 100 \mu\text{F}$ then value of $\tau = (1000\Omega) \times (100 \times 10^{-6}\text{F}) = 0.1 \text{ s}$. So, fully charged capacitor with initial voltage 10 V will take 0.1 s to drop it to 3.7 V and 0.5 s to discharge completely. The charging-discharging process of a capacitor is an important factor while considering dielectric capacitors as an option for pulsed power electronics (Jayakrishnan *et al.*, 2019a; Luo *et al.*, 2017). Fig. 4 shows the charging-discharging circuit diagram for a parallel plate dielectric capacitor.

Importance of Energy Storage Devices

There are many renewable and non-renewable sources of energy in nature to generate electrical power. The most common renewable sources of energy are solar, wind, ambient/mechanical vibrations in surrounding atmosphere etc. Due to the relatively lower power output and discontinuous character of these energy sources, the energy storage devices are generally used to accumulate and store the harvested energy for intermittent use. The conventional non-renewable ways of generating power through thermal, hydro, diesel, nuclear/atomic etc. usually generate huge power output. It is distributed to various public and commercial sectors through electricity grid transmission system which requires equal power supply and demand for its smooth functionality. The constant adjustments in power supply are always required for predictable changes in demand. The energy storage systems help in this balancing act. The storage of power is also required in many fields and applications to be used as and when needed. Thus, whichever be the power source, there is always a need and demand of ways to store the energy (Gür, 2018). Moreover, due to environmental concerns promoting the use of non-polluting electrical energy which majorly includes the electrification of various systems in commercial, non-commercial/civilian, and defense sectors necessitate the development of technological advanced energy storage devices (Palneedi *et al.*, 2018).

The different charging-discharging processes and energy storage mechanisms in devices (Fig. 5) makes significant difference in their energy density and power density outputs (Palneedi *et al.*, 2021). The Ragone plot (Fig. 6) compares the energy density and power density properties of most common energy storage devices (Han *et al.*, 2015; Palneedi *et al.*, 2018). For batteries, energy density is high but power output is too low due to its slow faradic process. It makes batteries a suitable source of stable energy supply for long-term. In electrochemical capacitors, the power density is improved with moderate energy density but still it takes few seconds to tens of seconds to charge/discharge (Palneedi *et al.*, 2018). The dielectric capacitors due to the inherent fast charging-discharging (Eq. 4) in dielectrics with discharge time in the range of μs to ms deliver a pulse output with high power density (Barber *et al.*, 2009). The solid-state dielectric capacitors could be operated at high voltage with long working lifetimes and, have better thermal and mechanical stability. These key features make them most suitable for energy storage applications in intense pulsed power systems.

Various Parameters Required to Evaluate Capacitive Energy Storage in Dielectrics

Stored and recoverable energy density

The work done by external voltage supply while charging a capacitor is stored as electrical energy. It is measured as stored energy density W_{st} which is given by relation

$$W_{st} = \frac{W}{Ad} = \frac{\int_0^{Q_{\max}} V \, dQ}{Ad}$$

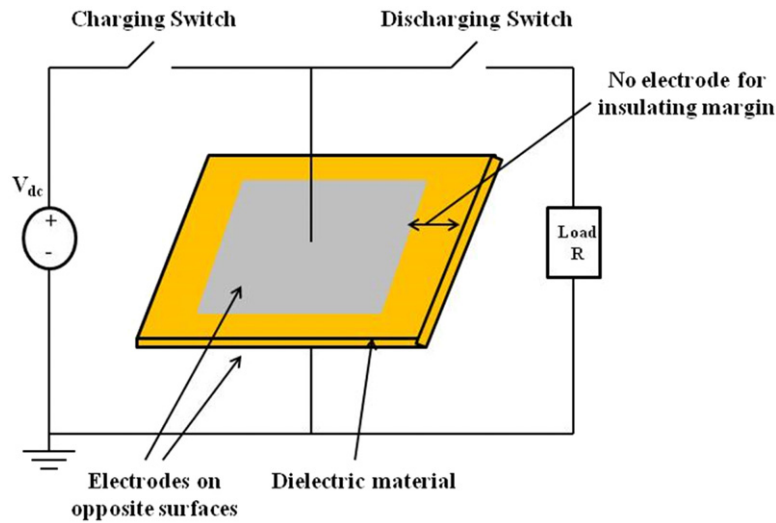


Fig. 4 Charging-discharging circuit diagram for a parallel plate dielectric capacitor. Adapted from Ref. Palneedi, H., Peddigari, M., Hwang, G.-T., Jeong, D.-Y., Ryu, J., 2018. High-performance dielectric ceramic films for energy storage capacitors: Progress and outlook. *Adv. Funct. Mater.* 28, 1803665. (1–33).

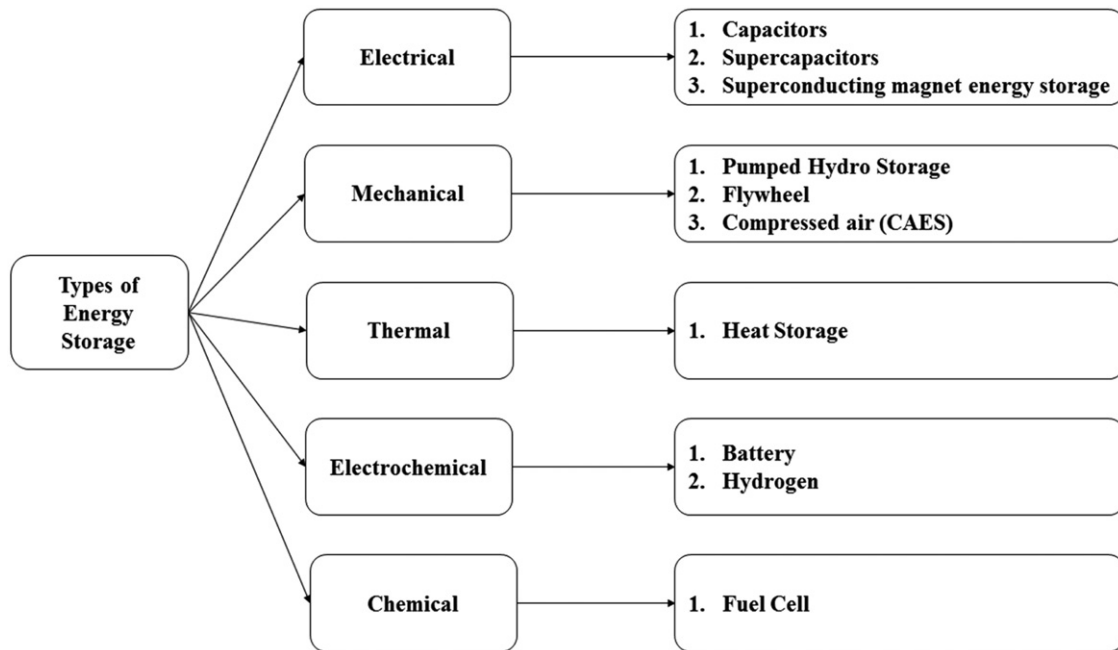


Fig. 5 Different types of energy storage systems/devices. Reproduced from Muqet, H.A., Munir, H.M., Javed, H., *et al.*, 2021. An energy management system of campus microgrids: State-of-the-art and future challenges. *Energies* 14, 6525.

In charged capacitor with dielectric medium, we have

$$\vec{E}_{eff} = \vec{E}_O + \vec{E}_P$$

$$E_{eff} = E_O - E_P$$

$$\text{As, } E = \frac{\sigma}{\epsilon_O}$$

$$E_{eff} = \frac{\sigma_f}{\epsilon_O} - \frac{\sigma_b}{\epsilon_O}$$

Where; σ_f and σ_b are the densities of free and bound charges respectively.

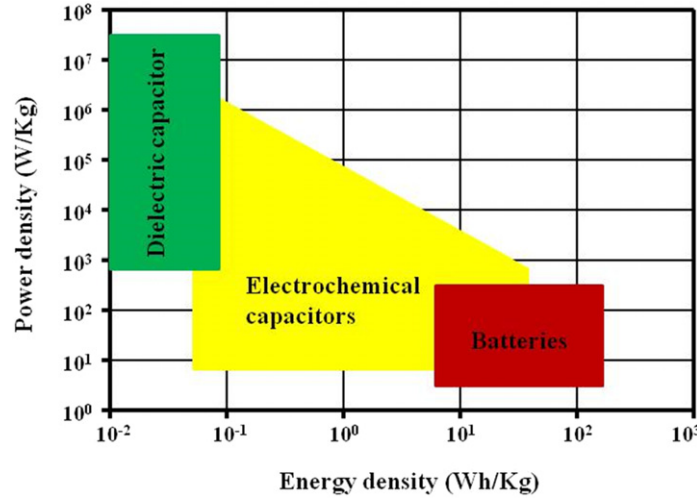


Fig. 6 Ragone plot comparing the energy density and power density capabilities of dielectric capacitors, electrochemical super-capacitors, batteries and fuel cells. Adapted from Refs. Han, F., Meng, G., Zhou, F., *et al.*, 2015. Dielectric capacitors with three-dimensional nanoscale interdigital electrodes for energy storage. *Sci. Adv.* 1 (1), e1500605. (1-6). Kötter, R., Carlen, M., 2000. Principles and applications of electrochemical capacitors. *Electrochim. Acta* 45, 2483–2498. Meng, C., Gall, O.Z., Irazoqui, P.P., 2013. A flexible super-capacitive solid-state power supply for miniature implantable medical devices. *Biomed. Microdevices* 15, 973–983. Also, permission to reprint from Ref. Palneedi, H., Peddigari, M., Hwang, G.-T., Jeong, D.-Y., Ryu, J., 2018. High-performance dielectric ceramic films for energy storage capacitors: Progress and outlook. *Adv. Funct. Mater.* 28, 1803665. (1–33).

$$\epsilon_0 E_{eff} = \sigma_f - \sigma_b$$

$$\sigma_f = \frac{Q}{A} = \sigma_b + \epsilon_0 E_{eff} = D$$

here, $D (= \epsilon_0 \epsilon_r E)$ is electrical displacement vector and $E = \frac{V}{d}$.

Thus, the stored energy density W_{st} is given by

$$W_{st} = \int_0^{D_{max}} E dD$$

$$\sigma_b = P$$

$$D = P + \epsilon_0 E$$

For linear dielectric materials,

$D \approx \epsilon_0 E$, thus the stored energy density W_{st} is expressed as

$$W_{st} = \frac{1}{2} \epsilon_0 \epsilon_r E^2 \quad (5)$$

In materials having large value of relative permittivity ϵ_r , D can be approximated to P . Thus for ferroelectrics, relaxor ferroelectrics, and anti-ferroelectrics non-linear dielectric materials, the expression for stored energy density W_{st} is given by relation

$$W_{st} = \int_0^{P_{max}} E dP \quad (6)$$

While discharging a capacitor, a part of total stored energy dissipated is called energy loss density W_{loss} and rest part is called recoverable energy density W_{rec} . The W_{rec} is expressed as

$$W_{rec} = \int_{P_r}^{P_{max}} E dP \quad (7)$$

For one charging-discharging cycle of a capacitor (**Fig. 7**), W_{loss} is measured by calculating the area under the P-E hysteresis loop and W_{rec} which is calculated as area above the P-E hysteresis loop. Hence, W_{st} can be expressed as $W_{st} = W_{rec} + W_{loss}$.

Energy storage efficiency

The practical use of dielectrics in energy storage capacitors not only require high energy storage density but also demand higher energy storage efficiency η . In terms of W_{st} , W_{rec} and W_{loss} , the relation for η is given by

$$\eta(\%) = \left(\frac{W_{rec}}{W_{st}} \right) \times 100 = \left(\frac{W_{rec}}{W_{rec} + W_{loss}} \right) \times 100 \quad (8)$$

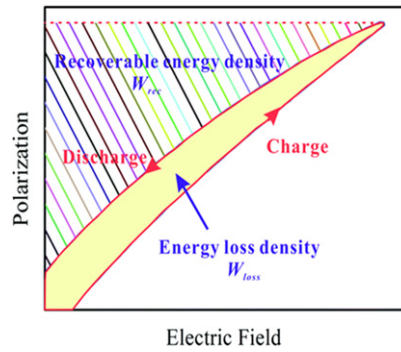


Fig. 7 Charging-discharging of dielectric material representing/showing the recoverable energy density W_{rec} and energy loss density W_{loss} . Reprinted with permission from Ref. Yang, Z., Du, H., Qu, S., *et al.*, 2016. Significantly enhanced recoverable energy storage density in potassium-sodium niobate-based lead free ceramics. *J. Mater. Chem. A* 4, 13778–13785.

The efficient energy storage capacitor requires low W_{loss} and high W_{rec} values. It can be achieved by the dielectric material having high ϵ_r and E_{BD} values, low dielectric and hysteresis loss, low value of remnant polarization P_r (i.e., slim ferroelectric hysteresis loop) and delay in saturation of polarization.

Dielectric breakdown field

The value W_{rec} for dielectrics depends on the induced polarization charge and the strength of electric field applied. For the materials with higher dielectric constant, it is easier for the valence electrons to become mobile. It means higher charge carrier density in such dielectrics can be attained on applying electric field. However, an avalanche multiplication of free charge carriers even at lower applied electric field leads to electrical breakdown in these materials, and hence the lower E_{BD} value. Prateek *et al.* (2016) has reviewed the dielectric properties of polymer and ceramic dielectrics. The ϵ_r of PVDF polymer is ≈ 10 (at 1 kHz) and its E_{BD} value is in the range of ≈ 1500 – 5000 kV cm^{-1} . For the barium titanate BT ceramics, the value of ϵ_r and E_{BD} is ≈ 1235 (1 kHz) and 150 kV cm^{-1} respectively (Prateek *et al.*, 2016).

The operating electric field of any dielectric capacitor depends on the intended application (Pirzada and Sabir, 2018). The E_{BD} of material strongly influences the reliability and the performance as dielectric capacitor. As both the charge induced and applied electric field effect the W_{rec} , there seems to be a situational decisive output or outcome in which the balance between ϵ_r and E_{BD} will lead to better energy storage density properties (Guo *et al.*, 2019).

Discharge time

For a fully charged capacitor, decay of charge and voltage drop across the capacitor is exponential and at any time t is expressed as in Eq. 4. The faster discharge of energy in dielectric capacitors is their unique characteristic.

We have

$$I = \frac{dQ}{dt} \text{ and Power} = I \times V$$

Thus the fast discharge in dielectric capacitor give rise to high current which results in high power (Palneedi *et al.*, 2018; Prateek *et al.*, 2016). The power density PD for dielectric capacitors can be calculated based on the recoverable energy density W_r via equivalent series resistance ESR and capacitance using the formula (Jayakrishnan *et al.*, 2019a; Luo *et al.*, 2017):

$$PD = \frac{W_r}{2 \times ESR \times C} \quad (9)$$

The ESR is considered as the product of capacitive reactance X_c and dielectric loss $\tan \delta$.

$$ESR = \tan \delta \times X_c = \frac{\tan \delta}{2\pi fC} \quad (10)$$

where f is the frequency of the applied signal and C is the capacitance. Therefore, the maximum power density can be calculated by the following:

$$PD_{\max} = \frac{\pi f W_r}{\tan \delta} \quad (11)$$

Fatigue endurance and thermal stabilities

For the low maintenance and the reliable use of dielectric capacitors for longer time, it should have better charge-discharge cyclic stability, mechanical and thermal stability. The endurance of dielectric capacitors to electric fatigue is usually determined by measuring or tracing the repetitive ferroelectric hysteresis loops at a constant electric field. The fatigue behavior in ferroelectric, relaxor-ferroelectric and anti-ferroelectric ceramic materials with high permittivity are possibly due to the changes in the formation and structure of crystals related to the relaxation of lattice-strain energy, long-range diffusion, and aggregation of defects, domain wall pinning, formation of low

permittivity dead layer between electrode/dielectric interface etc. (Palneedi *et al.*, 2018). With the increase in number of charge-discharge cycles the capacitance or the polarization of the dielectric material decreases which further degrades the energy storage capacity and performance of the dielectric capacitor (Guo *et al.*, 2019; Palneedi *et al.*, 2018; Prateek *et al.*, 2016).

The thermal stability of dielectric capacitors at higher temperature is also desirable for effective working with high maximum operating temperature in power electronics and other devices. Additionally to withstand heating-cooling thermal cyclic with variation in surrounding temperature due the operations over the long period, the heat generated by hysteresis energy loss and dielectric loss in the dielectric material also determine the energy storage properties/performance (Guo *et al.*, 2019; Palneedi *et al.*, 2018; Prateek *et al.*, 2016).

Dielectric Materials

Introduction

Based on electrical conductivity, the materials are classified into conductors, insulators and semiconductors. A dielectric material is an electrical insulator which polarizes on the application of electric field due to shifting and net displacement of positive and negative charge cloud. The positive charge shifts along the electric field and negative charge in direction opposite to field. This is called dielectric polarization. The displaced positive and negative charge constitutes a dipole which is the elementary unit of macroscopic net polarization P in dielectrics. The measure of separation of two opposite charges is called dipole moment and the magnitude of a dipole moment is expressed as:

$$\vec{p} = Q \times \vec{l} \quad (12)$$

where, Q is the magnitude of positive or negative charge and l is the length of dipole or distance between two charges. Every dipole in a dielectric material is like a vector whose direction is along the applied electric field (or from negative to positive charge of a dipole) and dipole density or macroscopic polarization P (C m^{-2}) is a vector field. Reversing the direction of electric field leads to depolarization and re-polarization of dielectric material in opposite direction. The dielectric insulators due to their property of being polarized are widely studied for their applications in various fields. The dielectric properties, to check the applicability of materials for specific application, generally vary with magnitude and frequency of applied electric field strength and the temperature of material. Gordon R. Love (1990) studied the ceramic dielectrics for energy storage applications and reported the maximum energy storage in materials with intermediate dielectric constant and the high breakdown voltages (Love, 1990). Since then a huge progress has been made in dielectric materials to understand the phenomenon and requirement for high energy storage, and developing techniques to tailor dielectric properties in materials of practical importance.

Classification of Dielectric Materials: According to Their Response to Applied Alternating Electric Field

When an alternating voltage is applied to a capacitor, it generates varying electric field inside the dielectric medium. In response to alternating electric field, the polarization, depolarization and re-polarization (polarization in opposite direction) of dielectrics lead to polarization-electric field P-E hysteresis loop. Depending upon the shape of P-E hysteresis loop and variation of permittivity with electric field, the dielectric materials are classified into linear dielectrics, paraelectrics, ferroelectrics, relaxor ferroelectrics and anti-ferroelectrics as shown in Fig. 9 (Su *et al.*, 2012; Tong *et al.*, 2013; Yang *et al.*, 2013; Yao *et al.*, 2017). Fig. 8 shows the orientation of electric dipoles in response to an electric field generated due applied alternating voltage leading to P-E hysteresis loop for a ferroelectric material (as an example).

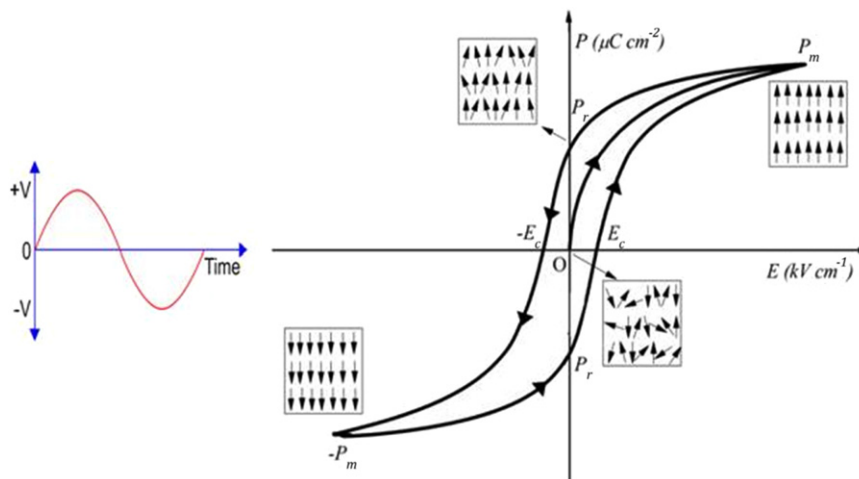


Fig. 8 One cycle of an alternating voltage supply leading to P-E hysteresis loop of a ferroelectric material with response of electric dipoles to generated electric field.

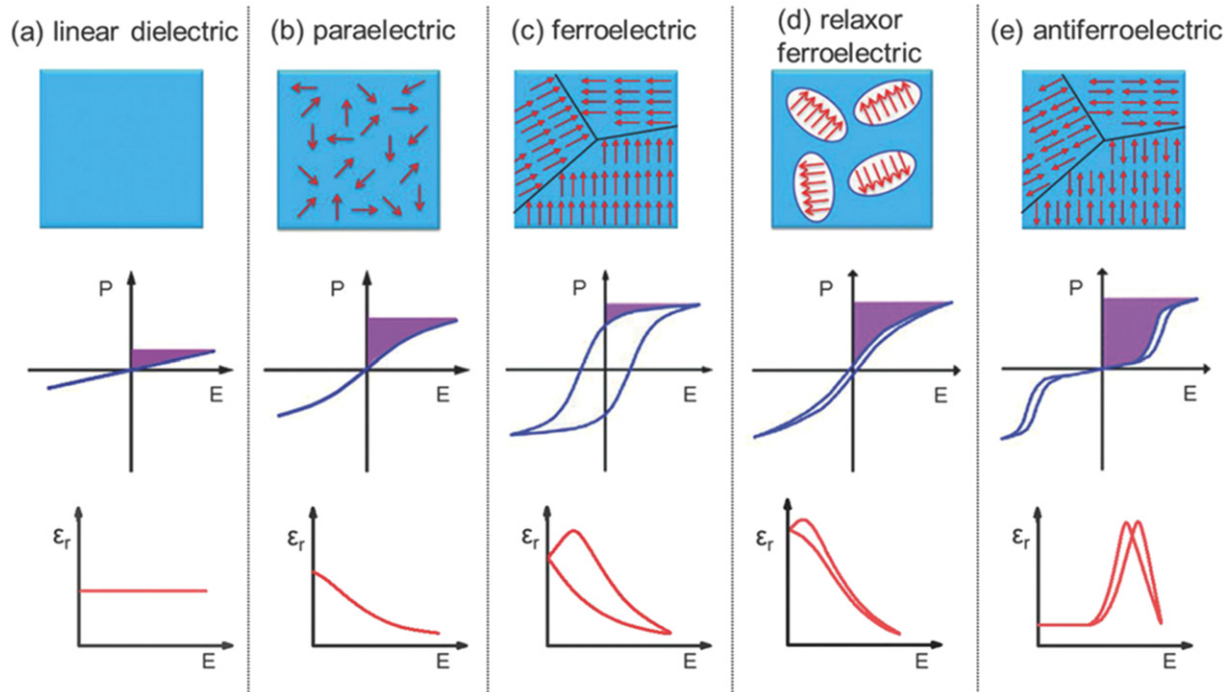


Fig. 9 Dipole and ferroelectric domain structure, dependence of polarization and permittivity on external electric field for (a) linear dielectric, (b) paraelectric, (c) normal ferroelectric, (d) relaxor ferroelectric, and (e) antiferroelectric dielectric materials. Reprinted with permission from Refs. Palneedi, H., Peddigari, M., Hwang, G.-T., Jeong, D.-Y., Ryu, J., 2018. High-performance dielectric ceramic films for energy storage capacitors: Progress and outlook. *Adv. Funct. Mater.* 28, 1803665. (1–33). Su, R., Tseng, J.K., Lu, M.S., *et al.*, 2012. Ferroelectric behavior in the high temperature paraelectric phase in a poly(vinylidene fluoride-co-trifluoroethylene) random copolymer. *Polymer* 53, 728–739. Tong, S., Ma, B., Narayanan, M., *et al.*, 2013. Lead lanthanum zirconate titanate ceramic thin films for energy storage. *ACS Appl. Mater. Interfaces* 5, 1474–1480. Yang, L., Li, X., Allahyarov, E., *et al.*, 2013. Novel polymer ferroelectric behavior via crystal isomorphism and the nanoconfinement effect. *Polymer* 54, 1709–1728. Yao, Z., Song, Z., Hao, H., *et al.*, 2017. Homogeneous/inhomogeneous-structured dielectrics and their energy-storage performances. *Adv. Mater.* 29, 1601727–1601741.

Linear dielectrics

The linear dielectrics illustrated in Fig. 9(a) usually are non-polar or weakly polar materials with low ϵ_r , high E_{BD} and, low W_{st} and W_{rec} values. In linear dielectrics, the energy density is directly proportional to ϵ_r and E_{BD} squared (Eq. 5) (Haitao and Scott, 2018). Nowadays, almost all the commercial polymer dielectrics used for energy storage are linear dielectrics. The low maximum polarization P_m in linear dielectrics limits the scope of enhancement in W_{rec} and their applicability in storage properties.

Paraelectric materials

Paraelectrics have no permanent dipole and there may be a formation of dipoles when an electric field is applied (Fig. 9(b)). These materials show weak polarization which disappears when field is removed. The strontium titanate (SrTiO_3) and its doped form are the most explored paraelectric materials for energy storage properties (Song *et al.*, 2014). Also, paraelectrics are combined or mixed with ferroelectrics and relaxor-ferroelectrics to enhance their energy storage by improving ΔP and E_{BD} values (as discussed later in chapter) (Jayakrishnan *et al.*, 2019a; Munir *et al.*, 2021; Wang *et al.*, 2022).

Ferroelectric materials

Ferroelectric materials (Fig. 9(c)) having strongly coupled dipoles form domains which lead to non-centrosymmetric displacement of dipoles and spontaneous polarization, as well as high dielectric constant within. Under the applied field the maximum polarization achieved in ferroelectric sample is called maximum polarization P_m . And, when the field is totally withdrawn, the sample retains some remnant polarization P_r owing to its intrinsic nature and thermodynamic conditions (Garg *et al.*, 2018). However, high remnant polarization results in a high loss during the energy storage, and the effective dielectric constant will reduce with the increase of the electric field. Some ceramics for example BaTiO_3 , PbTiO_3 , etc. are ferroelectric; PVDF is the most well-known ferroelectric materials in polymers (Jayakrishnan *et al.*, 2019b; Lovinger, 1983). Due to recent advances in synthesis techniques and better understanding of materials requirement for energy storage properties the normal ferroelectrics are tailored or artificially induced to perform better for capacitive energy storage applications.

Relaxor ferroelectrics

The relaxor-type behavior in some ferroelectrics is generally characterized by slim ferroelectric PE hysteresis loop which is further determined by low values of remnant polarization and coercive field. Such ferroelectrics have a diffuse and frequency dependent maximum value of permittivity, and a relaxation spectrum much broader than Debye-type (Bokov and Ye, 2012; Chen *et al.*, 2019; Cross, 1994; Jayakrishnan *et al.*, 2019b; Zhang *et al.*, 2017). Relaxor ferroelectrics generally have value of dielectric constant ($> 10,000$) higher than normal ferroelectrics, and the dielectric constant maxima at Curie temperature T_C much broader than normal ferroelectrics. The dielectric properties are more responsive to change in temperature, electric field and frequency (Zhang *et al.*, 2017). The significant feature of relaxor-ferroelectrics is the formation of polar nanoregions (PNRs) (Fig. 9(d)). The relaxor ferroelectrics are important for their applications in capacitive energy storage applications, due to their large saturation or maximum polarization P_m and small P_r values simultaneously i.e., $\Delta P = (P_m - P_r)$ is large. Different ideas to enhance its E_{BD} so that a large electric field can be applied and/or to maximize ΔP will consequently improve the W_{rec} and η properties in relaxors (Jayakrishnan *et al.*, 2019a, 2021). Different approaches such as doping and multi-layered heterostructures combining ferroelectrics with paraelectric materials have been employed to towards this (Jayakrishnan *et al.*, 2019a; Silva *et al.*, 2019). The operating electric field of any dielectric capacitor depends on the intended application (Pirzada and Sabir, 2018). However, to achieve large W_{rec} at lower applied electric field through the maximization of ΔP is also viable for many practical applications.

Antiferroelectrics

Antiferroelectricity (Fig. 9(e)) exists in materials with dipoles oriented in opposite directions. Some ceramics such as lanthanum-doped lead zirconate titanate PLZT have the antiferroelectric properties and were reported with a very high energy density indicated by the large area in Fig. 9(e) (Gao *et al.*, 2019; Palneedi *et al.*, 2018). The anti-ferroelectrics are also useful in energy storage applications due to their narrow P-E loop or large W_{rec} properties. However, the most of these are lead-based materials, which raise a serious environmental and human health concerns due to the high toxicity of the Pb.

Classification of Dielectric Materials: According to Their Permittivity and Electric Breakdown Strength Properties

Dielectric permittivity ϵ_r is the ability of the dielectric materials to respond to applied electric field. Materials having atoms with loosely bound electrons will respond faster to applied field and hence have higher permittivity. However, the dielectric breakdown strength E_{BD} is the property of dielectrics to withstand higher electric field. Dielectric materials with strongly bound valence electrons could withstand higher electric field and hence have high breakdown strength. In view of atomic structure of dielectrics, the ϵ_r and E_{BD} are the properties in contrast to each other and seems difficult to achieve simultaneously in a single-phase material i.e. materials with atoms having loosely bound electrons will have high ϵ_r but low E_{BD} , and vice versa. In view of ϵ_r and E_{BD} properties, the dielectrics can be categorized in to polymers, ceramics and glass materials.

Polymer-based dielectric materials

The polymer dielectrics are attractive for their easy applicability due to ease of fabrication to desired configuration, low-cost and ease of processing, and good thermal, chemical, mechanical and cyclic stability. The long molecular chains in the polymers provide them good mechanical flexibility. The electroactive polymers due to their high resistance and low dielectric loss break down electrically at much higher field values. That's why the polymers are supposed to have high E_{BD} value. However, due to low ϵ_r and limited maximum operating temperature limits the use of polymers for dielectric energy storage applications.

The ferroelectricity in polymers was first discovered in polyvinylidene fluoride PVDF in 1970s. Since then the progress in the polymer sciences has made a better understanding of phenomenon in polymers and enabled a better design of electroactive polymers with desired properties for electronic applications (Kawai, 1969; Li and Wang, 2016; Lovinger, 1983). PVDF and its copolymers, biaxially oriented polypropylene, polyethylene terephthalate PET, polycarbonate PC, polyimide PI etc. are the various dielectric polymers have been investigated for use in capacitor applications (Palneedi *et al.*, 2018). With the continuous progress in the field of electronics and electric industries, the polymeric materials are not enough to meet the ever increasing demand of new functional materials for applications in various fields (Lu *et al.*, 2017). For this purpose, generally to enhance the properties of polymers the organic, ceramic and carbon-based fillers are dispersed randomly in the polymer matrix (Amiri and Rahimi, 2016; Bhardwaj *et al.*, 2021; Lu *et al.*, 2017; Luo *et al.*, 2019; Men *et al.*, 2019; Patra *et al.*, 2018; Shepelin *et al.*, 2019; Thakur *et al.*, 2018). The polymer-nanocomposites are the most promising material-form in this regard.

Glass-based

The glass-based oxides are also explored for energy storage applications. The microstructure of these materials is characterized by the presence of crystallites held together by an amorphous glass matrix. The glass ceramics possess greater ϵ_r and much larger E_{BD} as compared to polymer dielectrics. However, the reported studies on their energy storage properties are less as compared to ceramics and polymers. The requirement of larger field intensities for high energy density raises the safety concerns. Moreover, at higher amplitude of applied voltages the possibility of corona leakage, electrical aging fatigue, insulation failure, and catastrophic dielectric breakdown pose the higher risk. The glass-ceramic systems based on barium titanate ($\text{BaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$, $\text{BaO-TiO}_2\text{-SiO}_2$), barium strontium titanate ($\text{BaO-SrO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$), alkali niobates ($\text{Na}_2\text{O-BaO-Nb}_2\text{O}_5\text{-SiO}_2$, $\text{Na}_2\text{O-K}_2\text{O-Nb}_2\text{O}_5\text{-SiO}_2\text{-B}_2\text{O}_3$) and other oxide glasses are studied for their energy storage applications (Hao, 2013; Palneedi *et al.*, 2018; Yang *et al.*, 2018; Yao *et al.*, 2017).

Ceramic-based dielectric

The dielectric ceramics are the most explored materials both in bulk and film form for their functionalities as capacitors in energy storage devices. The ceramics exhibit higher ϵ_r , but much lower E_{BD} in comparison to polymers. However, the significantly higher ϵ_r enable them to store the amount of energy of practical importance even at smaller applied fields. The higher thermal stability of ceramics is another exciting feature of these dielectrics (Guo *et al.*, 2019; Jayakrishnan *et al.*, 2019b; Luo *et al.*, 2018; Palneedi *et al.*, 2018; Wu *et al.*, 2016). The relaxor ferroelectric ceramic materials due to their slim P-E hysteresis loop has been widely explored for their applications in energy storage devices (Cowley *et al.*, 2011; Cross, 1994; Jayakrishnan *et al.*, 2019b; Shvartsman and Lupascu, 2012). The ceramic materials due to their enhanced functional electronic properties have proved their superiority in most of the applications in energy harvesting and storage devices, sensors, electrocaloric applications, memory devices etc. (Annapureddy *et al.*, 2016; Hwang *et al.*, 2016; Lakouader *et al.*, 2022; Maurya *et al.*, 2018; Palneedi *et al.*, 2016; Shi *et al.*, 2017b). However, the brittle nature of ceramics is a major concern. For this purpose, the various flexible solutions involving deposition of thin-films on flexible substrates and the ceramic nanofillers embedded in the polymer matrix were reported in past (Hwang *et al.*, 2016; Jain *et al.*, 2015; Li *et al.*, 2017; Mishra *et al.*, 2019; Tsege *et al.*, 2016). The dispersion of modest amount of ceramic nanofillers into polymer matrix is a feasible way to provide chemical, mechanical and thermal stability, and flexibility properties to ceramics of practical importance at the cost of best performance from them (Garg *et al.*, 2020; Lu *et al.*, 2017).

Ceramic-Polymer Nanocomposites

Introduction

The ceramic-polymer nanocomposites consist of polymeric materials as matrix and ceramic nano-inclusions. Among the available dielectric materials of all kind, the ceramics usually exhibit high ϵ_r ($\approx 10^2$ – 10^4) but low E_{BD} due to their structural imperfections. While polymers possess rather low ϵ_r (≈ 1 – 10) and high E_{BD} . For capacitive energy storage, both high ϵ_r and E_{BD} in dielectrics is favorable (Eqs. 6 and 7). High ϵ_r and E_{BD} are the two desirable but non-compatible properties due to the underlying physics behind it. These should be enhanced concomitantly to optimize the high recoverable energy density W_{rec} . The ceramics and polymers seems to be the dielectric material-forms with contrasting characteristic features in achieving the balance between ϵ_r and E_{BD} . Hence polymer nanocomposites are the emerging class of dielectrics which preserve the high E_{BD} of polymers and the enhanced ϵ_r due to the ceramic content. The progress in polymer nanocomposites facilitated the development of advanced materials for applications in capacitive energy storage devices.

The addition of ceramic nanoparticles with high ϵ_r into the polymer matrix having higher E_{BD} strength is a promising method to enhance of ϵ_r and E_{BD} concomitantly. Fig. 10 illustrates the variation of dielectric constant, dielectric breakdown strength, and energy density with variation in composition from pure polymers to bulk ceramics. As the components in the material-form changes from pure polymers to their composites, and to bulk ceramics, the dielectric constant increases and the breakdown strength decreases (Pirzada and Sabir, 2018). The sudden increase in the energy density property of dielectric polymer nanocomposites proves that this approach is feasible, particularly with the polymeric and inorganic ceramic phases facily integrated for capacitive energy storage applications.

In ceramic-filled polymer composites, the ceramic particles are interconnected to each other via polymer chains i.e., polymer matrix and ceramic particle interfaces exist while the ceramic particles break the continuity of long polymeric chains (Men *et al.*, 2019; Patra *et al.*, 2018; Reddy *et al.*, 2011). The network system in composites is entirely different from its components in their pure form i.e. grain boundaries form in bulk-ceramic and long molecular chains exist in a pure polymer (Dabra *et al.*, 2009; Nautiyal *et al.*, 2009; Reddy *et al.*, 2011; Reddy *et al.*, 2014). Hence, it would be interesting to explore how the polymer and ceramic influence and affect the properties of each other in composite systems. In past, various inorganic dielectric ceramics and polymers have been explored and optimized to get the outstanding properties at an individual level which somehow still lacks for the purpose of practical applications (Hong *et al.*, 2016; Koruza *et al.*, 2018; Yang *et al.*, 2015). The hybrid system is a concept which rather focuses more on the aspects of practical requirements at the cost of best from its different elements (de Oliveira Sousa Neto *et al.*, 2017; Nicole *et al.*, 2014). The introduction of massive ceramic nano-fillers near percolation threshold in polymer matrix greatly enhance ϵ_r but the dielectric E_{BD} and efficiency decrease severely. However, ceramic nano-fillers incorporated in small/optimized amount enhance the dielectric constant and breakdown strength simultaneously as observed. Hence, the dielectric constant, breakdown strength, and efficiency should be enhanced concomitantly for the overall improved performance in capacitive energy storage capacitors (Jiang *et al.*, 2021).

Various Basic Phenomenon Affecting the Dielectric Properties and Energy Storage Capacity of Ceramic-Polymer Composites

Polarization mechanism

In an external applied electric field, there is a shifting of net positive and negative charge cloud of an atom in dielectric material. The net displacement of charges constitutes an electric dipole and dipole moment is the measure of it. The total dipole moment

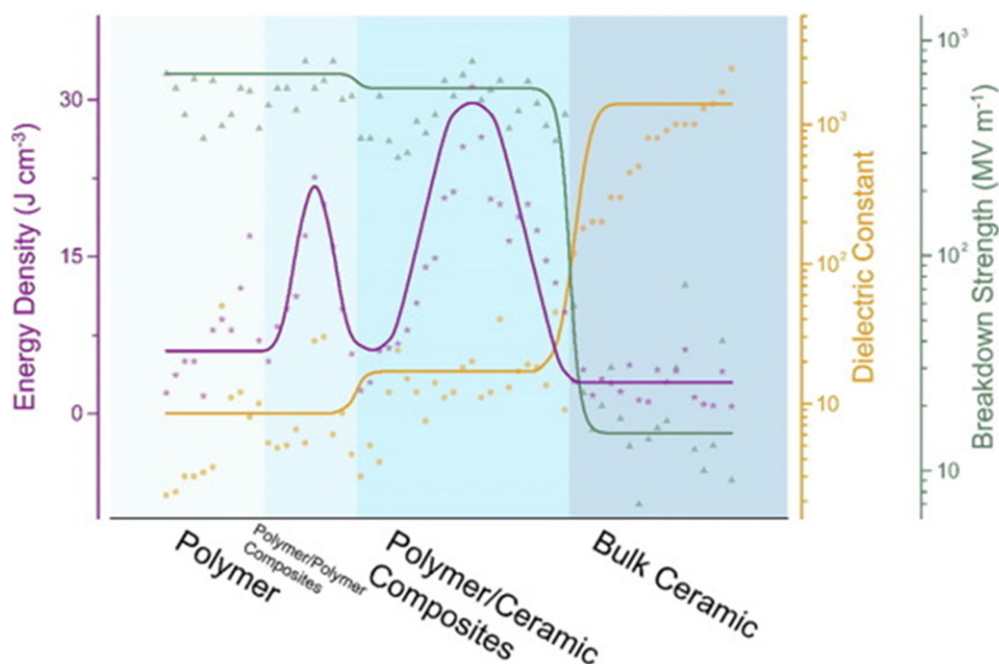


Fig. 10 The variation of dielectric constant, dielectric breakdown strength and energy density with changing phase components from pure polymers to composites to pure ceramics. Reprinted with permission from Ref. Guo, M., Jiang, J., Shen, Z., *et al.*, 2019. High-energy-density ferroelectric polymer nanocomposites for capacitive energy storage: Enhanced breakdown strength and improved discharge efficiency. *Mater. Today* 29, 49–67.

per unit volume of a dielectric medium or material is defined as polarization. Under the constant homogenous applied electric field, it is related to dielectric constant ϵ as $P = (\epsilon_r - 1) \epsilon_0 E$. Here, P is the net polarization developed in dielectric, E is the applied electric field, ϵ_r is the relative permittivity of material and ϵ_0 is the permittivity of free space (Prateek *et al.*, 2016).

In any dielectric material, mainly four types of polarizations occur. These are electronic, ionic, dipolar and interfacial (Fig. 11). Depending on the type of polarizing elementary unit in the dielectric medium or material, any of these polarization processes dominates. These polarizations can be further sub-divided into relaxation and resonance regimes (Zhu, 2014).

Electronic polarization: From the knowledge of basic atomic model, an atom comprises a dense positively charged nucleus at the center and a negative electron cloud around the nucleus makes an atom an overall neutral entity. In an externally applied electric field, due to the different nature of charge, the electron cloud displaces with respect to nucleus under the influence of field. This is called electronic polarization. The electronic polarization exhibits resonance for a narrow range at optical ($\approx 10^{15}$ Hz) frequencies (Fig. 11) (Kao, 2004).

Ionic polarization: The ionic materials/compounds consist of ions held together by electrostatic force which is termed as ionic bond. The ionic material/compound is overall electrically neutral having cation and anion with positive and negative charge respectively. When the lattice vibrations in an ionic material/crystal or molecular vibration induce the relative displacement of atoms of different kinds, the center of positive and negative charges also displaces (Kao, 2004). This is called ionic polarization. It responds in infrared frequency ($\approx 10^{13}$ Hz). For example, in sodium chloride crystal, the sodium ion (Na^+) and chloride ion (Cl^-) ions bound to each other via ionic bond form overall neutral crystal. The relative displacement between the two due to lattice vibration polarize it, is called ionic polarization.

In electronic and ionic polarization processes, the polarization due to relative displacement of opposite charges require a very little time and exhibit resonance in the narrow optical ($\approx 10^{15}$ Hz) and infrared ($\approx 10^{13}$ Hz) frequency range respectively. So, these are in the resonance regime of classification of type of polarization. These phenomena are intramolecular in nature and hence, are independent of temperature. The delocalization of electrons and the doping of elements in ionic materials are the fruitful ways to improve the electronic and ionic polarization (Pirzada and Sabir, 2018). However, the delocalization of electrons limits the improvement/enhancement in the dielectric properties of any material.

Dipolar/Orientational polarization: Orientational/dipolar polarization is observed in the polar materials having permanent polarization. A molecule or a part of molecule having net dipole moment is free to move under the influence of applied field. This is dipolar or orientational polarization. A molecule needs energy to overcome the resistance offered by surrounding to move/align with the applied field. Comparatively, the orientation of dipoles takes longer time in the range 10^{-6} – 10^{-9} s to perform. Hence, it lies in the relaxation regime of polarization. This is a temperature dependent phenomenon. The polymers with long molecular chain structure generally exhibit this kind of polarization. For example, in polyvinylidene fluoride (PVDF) the presence of highly polar C-F bond makes it electrically active. The arrangement of C-F bonds and their orientation with applied field defines the overall polarization.

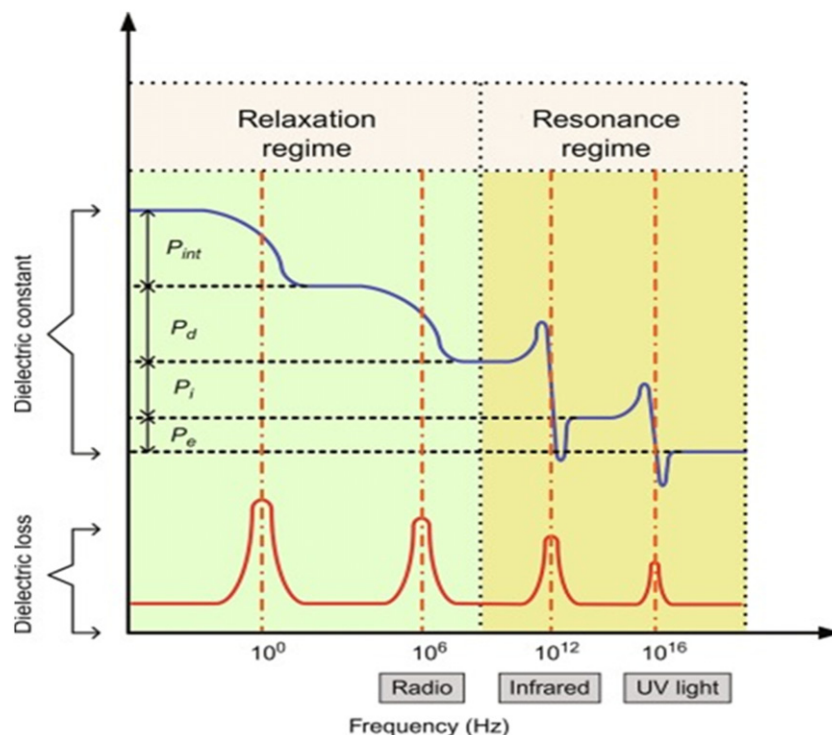


Fig. 11 Different type of polarizations and their frequency dependences. Reprinted with permission from Refs. Prateek, Thakur R.K., Gupta, R.K., 2016. Recent progress on ferroelectric polymer-based nanocomposites for high energy density capacitors: Synthesis, dielectric properties, and future aspects, *Chem. Rev.* 116, 4260–4317. Romasanta, L.J., Lopez-Manchado, M.A., Verdejo, R., 2015. Increasing the performance of dielectric elastomer actuators: A review from the materials perspective. *Prog. Polym. Sci.* 51, 188–211. Zhu, L., Exploring strategies for high dielectric constant and low loss polymer dielectrics. *J. Phys. Chem. Lett.* 5, 3677–3687.

Maxwell-Wagner-Sillars/Interfacial polarization: Interfacial polarization is due to the accumulation of charge at the interface of materials having different permittivity and conductivity or two regions of different permittivity and conductivity within a material. The non-homogeneity, presence of impurities, and incomplete metallic electrode contact with dielectric sample material leads to the regions of accumulated trap charges in the medium which further lead to polarization (Pirzada and Sabir, 2018). It is also called Maxwell-Wagner-Sillars interfacial polarization. The accumulated charge at the interfaces usually takes hours to years to discharge/relax. So, it too falls in the relaxation regime (Chanmal and Jog, 2012; Prateek *et al.*, 2016; Tuncer *et al.*, 2002; Yutao *et al.*, 1995; Zare and Rhee, 2020; Zhang *et al.*, 2016).

Loss mechanism

There are no losses for an ideal capacitor. However, in a real capacitor, generally two types of losses are present. First are the frequency-independent losses due to the conduction process involving long-range movement of charge or charge carriers following Ohm's law. And, second are the frequency-dependent dielectric losses. The dielectric losses are associated with the absorption of energy required for the movement of charge under the influence of applied field. In the long chain molecules in the polymeric materials, the dipolar or orientational polarization occurs. The dipolar group relaxation associated with the localized motion of molecules as well as the small chain units are known as β - and γ -relaxation respectively (Prateek *et al.*, 2016). Due to the micro-Brownian movement of the whole molecular chain or dipolar segment of molecule, the dielectric relaxation associated is known as α -relaxation. The different relaxation processes at different temperatures are illustrated in Fig. 12.

Breakdown strength

The E_{BD} of dielectrics is crucial in determining the maximum operational voltage for dielectric capacitors. Early breakdown is not desired for reliable usage of any dielectric material. The breakdown in solids could be electronic breakdown, thermal breakdown, electromechanical breakdown, insulation aging, internal and external discharges (Prateek *et al.*, 2016). The electric breakdown strength is somehow related to the ϵ_r of dielectric material. The materials having high ϵ_r break down early at low voltages. So, for the ceramic-polymer composites, the breakdown strength depends on the ϵ_r of individual ceramic/filler and polymer matrix component. A much contrast in the dielectric permittivity and conductivity properties of ceramic/filler and polymer matrix often lead to non-homogeneity of the field in the sample material which in turn effects E_{BD} (Guo *et al.*, 2019). The E_{BD} in composites can be enhanced by improving the bonding between two different phases ceramic as filler and polymer matrix (Wang *et al.*, 2014).

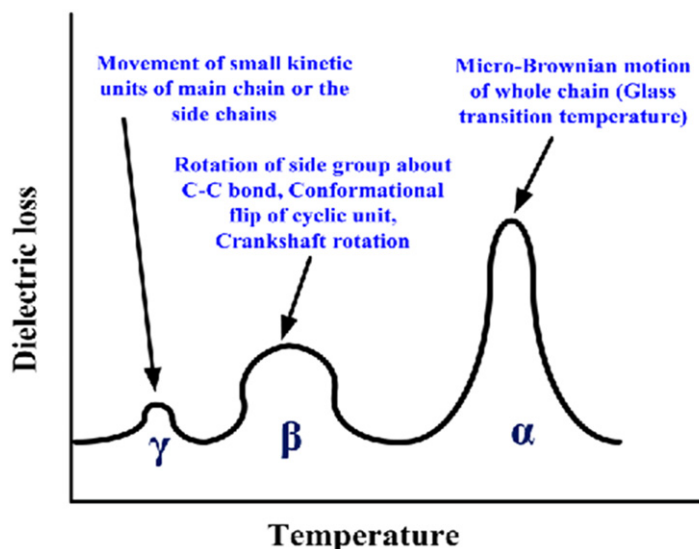


Fig. 12 Different relaxation processes at different temperatures. Reprinted with Permission from Ref. Prateek, Thakur R.K., Gupta, R.K., 2016. Recent progress on ferroelectric polymer-based nanocomposites for high energy density capacitors: Synthesis, dielectric properties, and future aspects, Chem. Rev. 116, 4260–4317.

For ceramic-polymer composite, the expression for electric field in filler E_f and polymer matrix E_m is:

$$E_f = E_o \left[\Phi_m \left(\frac{\epsilon_f}{\epsilon_m} - 1 \right) + 1 \right]^{-1}$$

$$E_m = E_o \left[\Phi_m \left(1 - \frac{\epsilon_m}{\epsilon_f} \right) + \frac{\epsilon_m}{\epsilon_f} \right]^{-1} \quad (13)$$

where; E_o and Φ_m are the magnitude of applied electric field and volume fraction of polymer matrix respectively. E_f and E_m are the electric field in the filler and polymer matrix respectively. ϵ_f and ϵ_m are the dielectric constant/relative permittivity of filler and polymer matrix respectively.

When the metals are used as fillers, E_f will be nearly zero and E_m will be sufficiently high. With such a field inhomogeneity in material the chances of early breakdown are more prominent. The breakdown strength can also be improved by homogeneous dispersion of fillers. The overloading of ceramic fillers is not an issue, even the inhomogeneous distribution at low loading level lead to conduction channel along the voids. So, the surface modifications can be applied to improve the breakdown properties and to extend the limit of filler loading in the polymer. The choice of polymer and filler are the most crucial in this (Prateek *et al.*, 2016).

Ceramic-polymer interface in composites

In ceramic-filled polymer composites, the ceramic particles are interconnected to each other via polymer chains i.e., polymer matrix and ceramic particle interfaces (Men *et al.*, 2019; Patra *et al.*, 2018; Reddy *et al.*, 2011). Depending on the type of dopant/filler nanoparticles, typically ranging from conducting to non-conducting, its incorporation into the polymer matrix affect the overall properties significantly. The polymer chain mobility, chain conformation, crystallinity etc. are the other factors reported to affect/control the interaction of filler nanomaterials with the polymer matrices. The Lewis's Model (Lewis, 1994, 2005) and the Tanaka's Model (Tanaka *et al.*, 2005) are the two important models hypothesized to explain the underlying phenomenon at the interfaces in ceramic-polymer nanocomposites materials. According to the Lewis's model, the difference in the Fermi levels of polymer matrix and filler nanoparticles induce charge on the surface of nanofillers. The polymer matrix in response develops counter charge near the nanofillers surface. It leads to redistribution of charge due to Coulomb attraction in the polymer matrix near nanofiller which results in formation of Stern layer and a Gouy-Chapman diffused layer (Fig. 13) (Lewis, 1994, 2005). The Stern layer is formed on the surface of nanoparticle due to the counterions. And further, the Stern layer is surrounded by diffused layer in the polymer matrix due to the distribution of charge. The diffused layer plays a major role in determining the dielectric responses/properties of polymer nanocomposites. It also becomes more predominant near percolation threshold of the fillers.

In another theoretical model proposed by Tanaka *et al.* (2005) (Fig. 14) to understand the phenomenon at interfaces in nanocomposites (Tanaka *et al.*, 2005). They considered the spherical dopant/filler nanoparticles being added into the polymer matrix. This model proposed the formation of interfaces in composites by the any of the chemical, physical or electrical process. Tanaka's model has assumed the formation of three bonded, bound and loose layers at the interface of filler nanoparticles and polymer matrix. The thickness of the first layer or bonded layer is ≈ 1 nm. It is strongly bonded to both inorganic nanoparticles and organic polymer via. either hydrogen bonds, van der Waals force or ionic or covalent forces. In the bound layer, the polymer

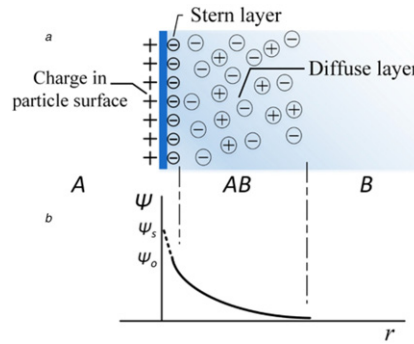


Fig. 13 Lewis double-layer model of interface a) The diffuse electrical double-layer model of a positively charged particle *A* in a matrix *B*, *AB* is its interface zone b) The resulting electrical potential distribution. Reprinted with permission from Refs. Lewis, T.J., 1994. Nanometric dielectrics. IEEE Trans. Dielectr. Electr. Insul. 1, 812–825. Lewis, T.J., 2004. Interfaces are the dominant feature of dielectrics at the nanometric level. IEEE Trans. Dielectr. Electr. Insul. 11, 739–753. Zhong, S.L., Dang, Z.M., Zhou, W.Y., Cai, H.W., 2018. Past and future on nanodielectrics. IET Nanodielectr. 1, 41–47.

chains are strongly bound/interact with bonded layer or the surface of nanoparticles. The thickness of bound layer is $\approx 2\text{--}9$ nm. The third or loose layer is loosely bonded with bound layer. In this layer/region, the different polymer chain conformations, mobility, free volume and crystallinity of polymer matrix effects the overall properties of dielectric ceramic-polymer composites (Prateek *et al.*, 2016).

Effective permittivity of ceramic-polymer composites

The effective permittivity of ceramic-polymer nanocomposites depend mainly on (a) the permittivity of individual component (ceramic filler and polymer matrix), (b) the wt% or amount of the individual component and, (c) the interactions among the different components (filler and polymer) in composites. Based on the different assumptions, various theoretical models have been proposed, developed and formulated to determine or calculate the effective permittivity of composites. The Lichtenker's formula, Maxwell-Garnett equation, Bruggeman Self-Consistent Effective Medium approximation and the Percolation theory are the various models are among these. The Lichtenker's formula is a logarithmic mixture formula and is most efficient in calculating the effective permittivity of the ceramic-polymer nanocomposites (Kiley *et al.*, 2012; Simpkin, 2010). It is expressed as

$$\epsilon_{eff}^{\zeta} = \Phi_f \epsilon_f^{\zeta} + \Phi_m \epsilon_m^{\zeta} \quad (14)$$

where; ϵ_{eff} , ϵ_f and ϵ_m are the effective permittivity of nanocomposites, permittivity of filler and polymer matrix respectively. Φ_f and Φ_m are volume fraction of filler and polymer respectively. ζ is value varying from -1 to $+1$.

The equation sets upper and lower limit of the permittivity of the mixture (Prateek *et al.*, 2016).

Different types of dielectrics: selection of proper polymer and ceramic material in view of energy density properties

The adoption of ferroelectric materials as piezoelectrics is the scientific advancement in the field of ferroelectricity. However, the key innovation in piezoelectrics was the development of piezoelectric composites by Newnham and Cross (Trolhier-McKinstry and Randall, 2017). The power figure of merit $d_h g_h$ for use of piezoelectrics in hydrophone applications was expressed as

$$d_h g_h = \frac{(d_{333} + 2d_{311})^2}{\epsilon_{33}} \quad (15)$$

where, ϵ_{33} is the relative permittivity and, d_{333} and d_{311} are the piezoelectric coefficients of material. The ϵ_{33} is quite large for most ceramics which lowers the value for $d_h g_h$. In 1978, Newnham and Cross formulated the idea of utilizing the connectivity of two different phases in piezoelectric composites to gain properties that were inaccessible in single-phase materials for the use of piezoelectrics in hydrophone applications. Fundamentally, his motivation was to lower the ϵ_{33} value by combining ferroelectric ceramic with a soft polymer in composites and hence improve the $d_h g_h$ value. A similar approach is generally followed in the selection of materials to improve the properties of ferroelectric composites accordingly for designing devices in various applications (Doagou-Rad *et al.*, 2020).

For capacitive energy storage, both high ϵ_r and E_{BD} in dielectrics is favorable (Eqs. 6 and 7). High ϵ_r and E_{BD} are the two desirable but non-compatible properties due to the underlying physics behind it. Hence the addition of ceramic nanoparticles with high ϵ_r into the polymer matrix having higher E_{BD} strength is a promising method to enhance of ϵ_r and E_{BD} concomitantly (Fig. 10). Moreover, ceramics with relaxor-type ferroelectricity are ideal energy storage due their slim hysteresis loop leading to efficient energy storage.

Other factors affecting the overall electrical properties of ceramic-polymer nanocomposites in view of properties of individual component and their phase compatibility:

Ceramic or filler nanoparticles: The composition and size of ceramic/filler nanoparticles affects its ferro/piezoelectric properties.

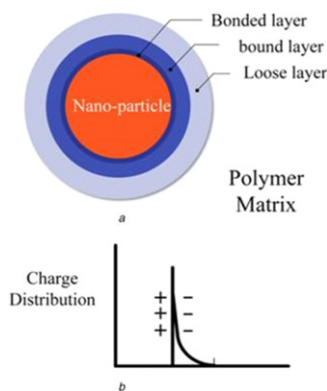


Fig. 14 Tanaka multi-core model of interface (a) Multi-core model for nanoparticle/polymer interface (b) Charge distribution of the corresponding multi-core model, supposed the nanoparticle is positively charged. Reprinted with permission from Refs. Tanaka, T., Kozako, M., Fuse, N., Ohki, Y., 2005. Proposal of a multi-core model for polymer nanocomposite dielectrics IEEE Trans. Dielectr. Electr. Insul. 12, 669–681. Prateek, Thakur R. K., Gupta, R.K., 2016. Recent progress on ferroelectric polymer-based nanocomposites for high energy density capacitors: Synthesis, dielectric properties, and future aspects, Chem. Rev. 116, 4260–4317. Zhong, S.L., Dang, Z.M., Zhou, W.Y., Cai, H.W., 2018. Past and future on nanodielectrics. IET Nanodielectr. 1, 41–47.

Electroactive polymer: The PVDF phase stabilization is effected by processing technique and doping in polymer matrix. The electric properties of PVDF highly depend on its phase stabilized.

Interfacial bonding: The ceramic-polymer phase compatibility or interactions at interface influence the overall properties of composite materials.

Other controlling factors: The processing technique affecting the degree of mixing and morphology of sample materials and, wt% of ceramic and polymer phases in composites are the other factors controlling/affecting the overall dielectric properties of composites.

Synthesis and Characterization Techniques: In View of Ceramic-Polymer Nanocomposites

Nanoparticles Synthesis

Over the period of few decades, many methods have been reported for synthesis of metal oxides materials (Niederberger, 2007; Zhang *et al.*, 2016). The conventional solid-state reaction method has been the most frequently used method for the production of complex oxides due to its simplicity. It involves the mixing of simple oxides, carbonates, hydroxides, and other metal salts, several milling and annealing steps to get homogeneous mixture with smaller particle size. But due to the high temperatures requirement in this method which generally results in the formation of coarse particles (in μm range), along with the emergence of undesirable phases due to decomposition of the product formed and impurity in phase due to repeated grinding (Buekenhoudt *et al.*, 2010; Wu *et al.*, 2016). The softer chemical solution derived (CSD) processes are gaining momentum to synthesize metal oxides especially nanocrystalline oxides to attain a well control over the stoichiometry, particle shape and size, uniformity and purity of phase, and structural properties. The basic approach aims to use simple chemical reactions like sol-gel, co-precipitation, hydrolysis, acid leaching, ion exchange etc. and that too at extensively low temperatures compared to the conventional ceramic method. Hydrothermal synthesis is quite advantageous in that the particle size and material morphology can be controlled along with improved product homogeneity (Hanani *et al.*, 2020b; Zhang *et al.*, 2016). Sol-gel synthesis is considered a soft route using low temperatures to achieve uniform products. The product morphology can be controlled through process conditions (temperature, pH, pressure, type of solvent/mineralizer etc.) with the possibility of producing small particle sizes with suitable crystallinity (Hao *et al.*, 2017). Like many methods, sol-gel routes are time consuming due to multistep processes and, also require costly reagents. However, sol-gel synthesis addresses many of the above concerns and considered to be both a time and energy efficient process.

SOL-Gel method

The sol-gel is one of the most common methods used to synthesize the metal oxides based 0-D, 1-D, 2-D nanostructures and thin films (Hench and West, 2002; Zhang *et al.*, 2016; Chandler *et al.*, 2002; Garg *et al.*, 2021; Garg *et al.*, 2020; Thompson and Carel, 1996). The first and the most crucial step in the whole process of sol-gel technique is the formation of chemical solution containing all the required metal ions dissolved in a suitable solvent. The solvent evaporates during the heating process and the metal ions crystallize to form the final structures. Hence, the solution acts as a precursor for the synthesis of desired material regardless of their form and structure. It is also called a precursor solution. The precursor solution due to its liquid nature can be casted into range of morphologies in its final form simply by using an appropriate template for nanostructures and different deposition techniques for thin films. A good precursor solution having stoichiometric metal sources, a suitable solvent and appropriate chelating agent are the key factors for the synthesis of material in desired final-form. Hence, it is evident that a good

precursor solution, the chemical reactions between its ingredients and, the heat treatment processes strongly influence the ultimate quality of the final material (Zhang *et al.*, 2016).

Auto-combustion synthesis

The auto-combustion synthesis comprises the exothermic reaction between metal nitrates and a fuel in precursor solution. It utilizes oxidizer(s) and organic fuel mixed in an aqueous solution. Metal nitrates are commonly used oxidizers because they are water soluble. During the combustion process, the organic fuel (e.g., urea, citric acid, glycine, mono-ethanolamine etc.) is widely exploited due to ease of availability and high exothermicity (Kaur *et al.*, 2019, 2016). The fuel serves as a source of carbon and hydrogen atoms generating carbon dioxide and water. The overall SCS process involves mixing of stoichiometric amounts of the metal nitrate and organic fuel in solution and then dehydrated, ignited, and finally combustion of the precursors is carried out (Kaur *et al.*, 2019, 2016). To trigger the ignition of exothermic redox reaction heat is required which is typically supplied by an external heating source. It follows the combustion reaction which leads to the crystallization of material during the continuous heating process involved in the reaction. During the onset of the combustion reaction, the generated exothermic propagating wave endorses high product crystallinity. The ejection of gases results in finely dispersed, porous solid particles of high purity. Short reaction time hinders the increase of particle size, thus favoring nano-sized material (Kaur *et al.*, 2016; Jasrotia *et al.*, 2020; Kaur *et al.*, 2019, 2016; Mukasyan and Dinka, 2007).

Hydrothermal synthesis

The boiling point of any liquid is the temperature at which vapor pressure equals the atmospheric pressure. The hydrothermal synthesis is preparation method to synthesize good quality material crystals in hot water or solvent under high pressure at temperature much higher than the boiling point of water or solvent. Hydrothermal synthesis offers a control on final quality and morphology of the crystals by simply tuning the ions and their concentration in solvent and, the temperature and pressure under which the ionic reaction equilibrium have built. It involves the formation of precursor solution by dissolving metal sources such as metal nitrates in deionized water or nitric acid. The sodium hydroxide *NaOH* or potassium hydroxide *KOH* is the most reported mineralizer to control the crystal size of the nanomaterial/nanostructures during synthesis. The precursor solution is then poured into the Teflon jar which is placed in a stainless-steel pressure vessel called autoclave. The autoclave is maintained at temperature ($\approx 200^\circ\text{C}$) in oven for optimized time ($\approx 10\text{--}15$ h). On cooling, the material crystals are filtered and dried. The mineralizer, temperature and pressure are the parameters which generally effects the crystal quality, size and structure (Hao *et al.*, 2017). The volume % of precursor solution to be filled in the Teflon jar and the operational temperature of hydrothermal autoclave are the most important parameters to note for the cautious operation of hydrothermal reactions.

Microwave-hydrothermal synthesis

The modified form of hydrothermal synthesis with some modifications in the process of heat-treatment is called microwave-hydrothermal synthesis. The procedure for the formation of precursor solution is same but for heating process, the microwave heating techniques are used. The Teflon autoclave is put in microwave oven. Generally, it takes 0.5–1 h for the whole reaction process which takes long time of 5–72 h in traditional hydrothermal synthesis process (Zhang *et al.*, 2016).

Synthesis of Pure Polymer and Ceramic-Polymer Nanocomposites

The composites of ceramics and polymers are prepared by the dispersion of ceramic nanoparticles in to the polymer matrix. The preparation technique typically includes the mixing of two different phases either by a chemical or mechanical process. The dispersion of nanofillers uniformly and homogenously in the preparation of polymer nanocomposites is most challenging. The major problem encountered was the tendency of nanofillers to aggregate and form filler cluster of micron size. The formations of ceramic clusters separate the phases in composites thereby deteriorating the overall properties of nanocomposites. It also limits the scope of enhancement in properties of polymer by limiting the dispersion of nanofillers/particles in the polymer matrix. The research work in polymer science have made many attempts for uniform and homogenous dispersion of nanofillers in the polymer matrix induced by chemical reactions, complicated reactions of polymerization process and by employing surface modifications on filler nanomaterials (Tanahashi, 2010). The polymer matrix nanocomposites preparation techniques are mostly categorized in to following four methods.

Intercalation method

It is a top-down approach in which two material phases with known properties are just mixed to get the new material-form having desired properties. The intercalation method generally involves dispersing the platelet-nanofillers into the polymer matrix. The intercalated morphology happens by the diffusion of polymeric chains into the spacing between the layered structures of platelet nanofillers. Intercalation method requires the modification on the filler nanoplatelets surface for the homogenous dispersion of plate-like fillers into the polymer matrix. Intercalation is generally done by following chemical technique (in-situ polymerization), mechanical technique (direct intercalation) or melt-intercalation method (Alexandre and Dubois, 2000; Hamadneh *et al.*, 2016).

IN-situ polymerization method

The nanofillers are dispersed into the monomer solution in in-situ polymerization method. Due to the low molecular weight of the monomer solution, it seeps easily into the layer/space between the nanofillers. The resulted mixture is then polymerized using either radiation, heat, initiator diffusion or organic initiator (Hamadneh *et al.*, 2016).

SOL-GEL method

The sol-gel method is a bottom-up approach in which the cross-linking or polymerization reaction in solution results in composite formation. The dispersion of solid nanoparticles/fillers into the monomer solution involved in sol-gel method form a colloidal suspension of solid nanoparticles called sol. Through the process of polymerization in solution, an interconnecting network between the different phases forms a gel. The formation of gel is followed by hydrolysis reactions. The three dimensional interconnecting network between the polymer and nanoparticle/filler extend throughout the mixture with time. Here, a nucleating agent is polymer which promotes the formation of layered structure. As the structure grows, the polymer seeps into the layer/space between the nanofillers and nanocomposite forms (Hamadneh *et al.*, 2016; Reddy, 2010).

Direct mixing of polymers and nanofillers

The polymers and nanofillers of known properties are mixed directly to form composite material-form having distinct properties. The direct mixing of polymer as matrix and ceramic nanoparticles as fillers is a top-down approach for the preparation of nanocomposites. This technique is based on the principle of breaking the cluster of aggregated nanofillers during the mixing process which forms ceramic-polymer composites with uniformly and homogeneously dispersed nanofillers into the polymer matrix (Tanahashi, 2010). It is the most suitable technique for the preparation of polymer matrix nanocomposites, and generally involves the two ways of mixing solid nanofillers/particles and polymer (Jiang *et al.*, 2017). One-way is mixing nanofillers in polymer is by heating a polymer at temperature above its glass transition. The nanofillers will be dispersed in polymer in its melt state (Garg *et al.*, 2021). It is generally called melt-compounding method. The second way involves the mixing of polymer and nanofillers in a solution employing solvents (Garg *et al.*, 2021, 2020). It is generally known as solvent method or solution mixing (Hamadneh *et al.*, 2016; Reddy, 2010).

Melt-press method

It is a direct mixing of polymer and nanofiller technique involving the addition of nanofillers into the polymer matrix at temperature above the glass transition temperature of a polymer. The polymer and nanoparticles were grounded well in mortar-pestle ensuring the proper mixing of different phases and the breakdown of clusters of aggregated nanofillers during the mixing process. While heating the mixture, the shearing stress or the hydrodynamic force is induced during the melting of polymer by a viscous drag. The resulted shear stress breaks the aggregation of nanoparticles and, thereby promotes the uniform and homogeneous dispersion of nanofillers in the polymer matrix (Garg *et al.*, 2021; Hamadneh *et al.*, 2016; Kumar *et al.*, 2013; Reddy *et al.*, 2011). Fig. 15 schematically shows the general methodology for melt-press technique.

Solution-cast method

In this method of direct mixing of polymer and nanofillers, the polymer is dissolved in a suitable solvent and then, the solid nanofillers are dispersed in the polymer solution. The nanofiller polymer solution is sonicated several times to ensure the breakdown of nanofiller aggregate. The resultant nanocomposite is recovered from the nanofiller polymer solution by solvent evaporation (Hamadneh *et al.*, 2016; Patra *et al.*, 2018; Shi *et al.*, 2017a; Tong *et al.*, 2019). Fig. 16 schematically shows the general methodology for solution-cast technique.

Characterization Techniques

The structural, dielectric, ferroelectric and storage energy density properties of ceramic-polymer nanocomposites are generally studied to characterize their applicability in dielectric energy storage.

Structural properties

X-ray diffraction (XRD)

The X-ray diffraction (XRD) is a technique used to study the structural arrangement of atoms or molecules in a crystalline material. The principle of XRD technique is that when a beam of monochromatic light having wavelength of the order of the interatomic distance of the sample material to be irradiated, then the crystalline structure causes a beam of incident light to scatter elastically in many specific direction. The scattered light undergoes diffraction phenomenon and, by measuring the diffraction angles and intensities of diffracted beams the pattern of intensity distribution with angle is formed. It is called the XRD pattern of sample crystalline material. The XRD pattern is correlated to the arrangement of atoms in the material. The wavelength of X-rays used to produce the diffraction pattern of sample materials is $\approx 1\text{--}100\text{ \AA}$ which is typically the same order of d -spacing between the crystalline planes. If the wavelength of incident X-ray from the source is λ and θ is the glancing angle of incidence, then the constructive interference of transmitted X-rays will be observed at an angle 2θ from the direction of incident beam. The λ , θ and d_{hkl} must satisfy the Bragg's condition for the occurrence of constructive interference (Cullity, 1956; Muniz *et al.*, 2016; Patterson,

MELT – PRESS TECHNIQUE

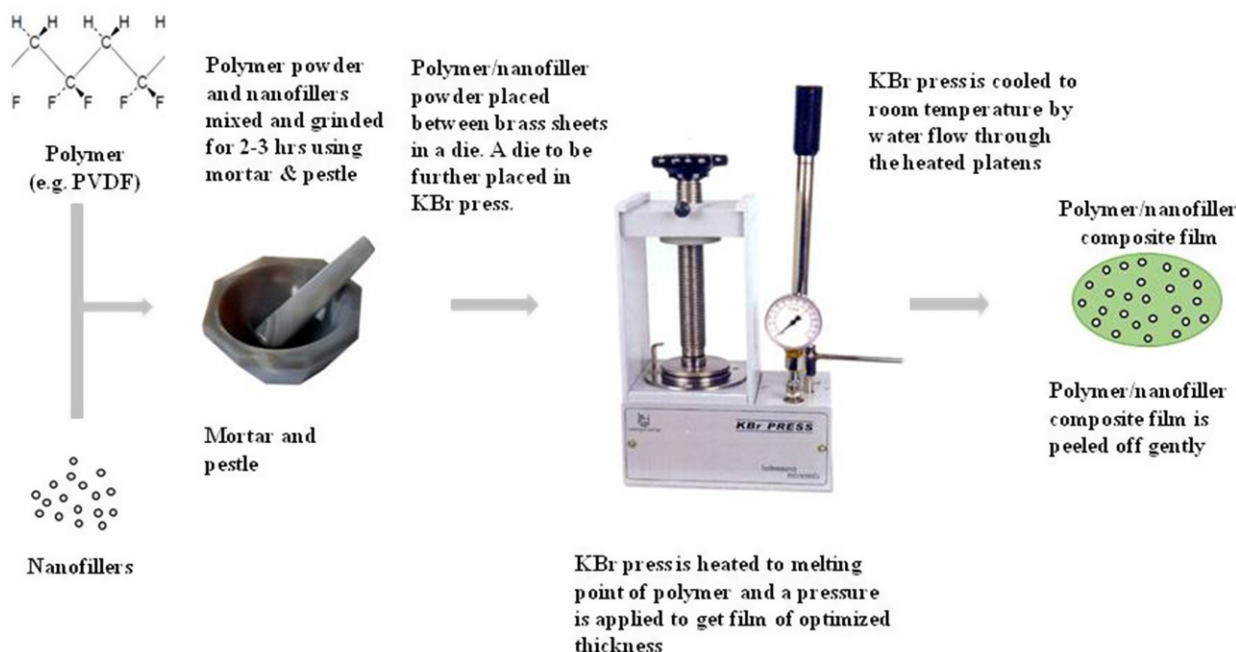


Fig. 15 General methodology for Melt-press technique.

1939). The Bragg's equation for the occurrence of diffraction maxima is

$$2d_{hkl}\sin\theta = n\lambda \quad (16)$$

where d_{hkl} is the D-spacing of parallel diffracting planes represented by hkl-miller indices, θ is the Bragg's angle and n is the diffraction order.

It is worthwhile to mention here that the mean crystallite size of nanomaterials can also be obtained from the XRD spectrum using Scherrer's equation (Cullity, 1956; Muniz *et al.*, 2016; Patterson, 1939). The smaller domains within each crystal or grain are called crystallites. And, crystals form the particle. The XRD technique is so powerful that it identifies the crystallites or rather calculates the average size of these crystallites (Garg *et al.*, 2020). The information regarding the identification of the material and its crystalline phase can also be obtained. The Scherrer's equation can be written as:

$$\tau = \frac{K\lambda}{\beta \cos\theta} \quad (17)$$

where; τ is the mean size of crystallite, which may be smaller or equal to the grain size, which may be smaller or equal to the particle size. K is Dimensionless shape factor whose value is about 0.9 but varies with the actual shape of crystallite. λ , β and θ are the wavelength of X-ray, line broadening at FWHM (in radians) and Bragg's angle respectively.

Fourier transform infrared spectroscopy (FTIR)

The spectroscopic techniques are the primary tools to unveil the structure of the compounds and are based on the molecular interaction of electromagnetic radiations with the electromagnetic fields of the charge entities present in the compound. Spectroscopy exploits the fact that molecules absorb frequencies that are characteristic of their structure. The different energy range of electromagnetic spectrum show resonance with corresponding energy transitions inside the molecule. Infrared radiation is an electromagnetic radiation with wavelength in the range 780–1000 μm . The infrared energy range shows interaction with vibrational and accompanying energy states of the molecule and provides information about the presence of characteristic vibrational bands and hence helps in identifying the structure of the molecule (Gaffney *et al.*, 2012).

The infrared spectroscopy (IR) is widely used in characterizing sample material under study. In this technique, the infrared radiation is passed through a sample material, the part of which is absorbed by the sample and the rest is just transmitted. If the absorbed and transmitted is being observed, the resulting plot of variation in absorption or transmission of radiation with its wavelength or frequency is the IR spectrum. It represents the molecular absorption or transmission, creating a molecular fingerprint of the sample. In a molecule making up the material, the bonds of the atoms have the characteristic frequencies of vibrations.

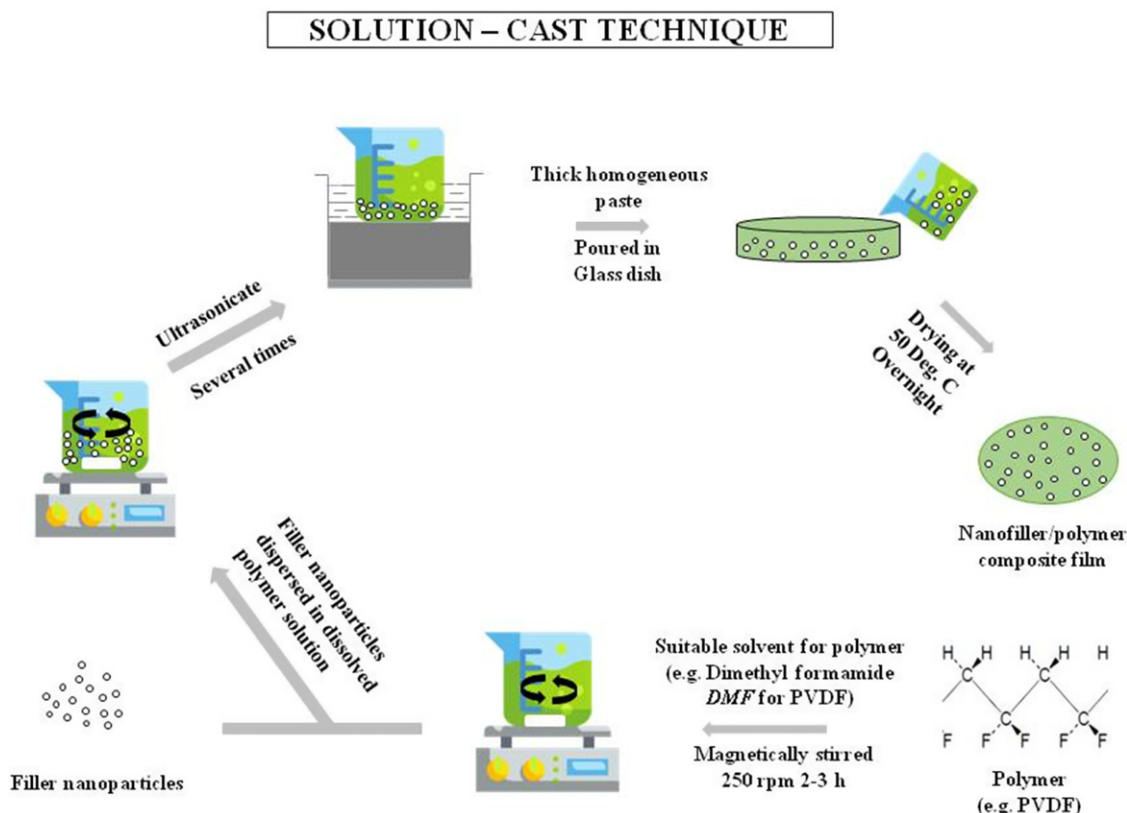


Fig. 16 General methodology for Solution-cast technique.

In the IR spectra, the absorption peaks corresponds to that characteristic frequency of the bonds. The set of positions of absorption peaks in the IR spectra is unique for sample material. Hence, the infrared spectrum represents the fingerprint of sample. It means no two compounds will produce the similar IR spectra as the different materials have a unique combination of atoms and nature of bonds between them (Cai *et al.*, 2017; Gaffney *et al.*, 2012).

The Fourier-transform infrared spectroscopy (FTIR) measures the infrared absorption and transmission by a sample material as a function of wave number (λ^{-1}). In FTIR, instead of shining a sample material with monochromatic beam of light, a beam containing radiations of different frequencies shines on sample and measures the absorption and transmission of each frequency radiation. The next modified beam containing the different frequency combinations gives the second data point. This is repeated over a short interval of time between the desired frequency ranges. The collected IR raw data is processed computerized to get the complete desired data or spectrum. The processing algorithm called Fourier Transform inverts the one domain and, results absorption and transmission spectra with wavenumbers (λ^{-1}). Hence, it is called FT-IR spectrum. In FTIR spectroscopy, the identification of absorption bands is associated with the vibrations of particular functional groups at characteristic frequency within a molecule. The identification of bonds results in the identification of molecules of the material under investigation. This technique is generally used for identification of compound, their structural clarification, quantitative analysis of one or more known species in sample material, and to measure the fundamental properties of a molecule (Cai *et al.*, 2017; Garg *et al.*, 2021; Garg *et al.*, 2020; Karan *et al.*, 2019; Lu *et al.*, 2017; Mohanty *et al.*, 2019b; Sharma *et al.*, 2018; Tashiro *et al.*, 1981). However, the compound identification is still the first and most important application of FTIR spectroscopy. Today, the FTIR spectroscopy is implemented to all types of organic and most of the inorganic materials over the wide range of their sample forms including gases, liquids, bulk and powdered solid samples, thin films and nanomaterials.

Dielectric properties

Dielectric properties are important to study the applicability of material in capacitive energy storage. The capacitance C and loss tangent $\tan \delta$ of sample capacitor were measured with variation in frequency and temperature using Impedance Analyzer. A small ac signal of amplitude 1 V was applied to the sample capacitor and impedance analyzer linked to a computer via a GP-IB (general purpose interface bus) interface was used for measurements. The expression to evaluate relative permittivity ϵ_r from the recorded capacitance for a sample material capacitor of known area A and thickness d is given by relation

$$\epsilon_r = \left(\frac{Cd}{A} \right) \left(\frac{1}{\epsilon_0} \right) \quad (18)$$

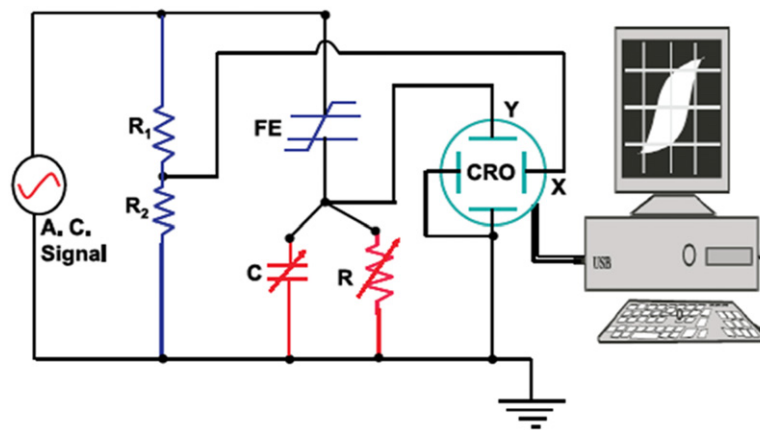


Fig. 17 Sawyer Tower circuit for PE loop measurements. Reproduced from Zheludev, I.S., 1971. *Physics of Crystalline Dielectrics*, Physics of Crystalline Dielectrics. Springer.

where; ϵ_0 is the dielectric constant of free space ($\approx 8.85 \times 10^{-12}$ F/m). C , A and d are the capacitance (as recorded by the instrument), area and thickness of sample.

Ferroelectric properties

P-E hysteresis loop is a significant feature of ferroelectric behavior of dielectrics. The P-E measurements are important because the existence of loop together with the reversal of spontaneous polarization on application of alternating electric field is commonly accepted as a proof of ferroelectricity. A good ferroelectric material exhibits a relatively saturated P-E loop. The value of remnant polarization P_r and coercive field E_c from the P-E loop generally measure the ferroelectric behavior and, the area calculations in the P-E diagram measures the storage energy density properties of any dielectric material. The overall P-E hysteresis loop shape, area, and the values of P_r and E_c depend on the dielectric behavior of material and its energy storage capacity.

The endurance of dielectric capacitors to electric fatigue is usually determined by tracing the repetitive ferroelectric hysteresis loops at a constant electric field. Tracing P-E loops at higher magnitude of electric field without short circuiting the dielectric material under study also measures its dielectric breakdown strength properties.

The P-E hysteresis loop of ferroelectric material can be obtained using the Sawyer-Tower circuit (Fig. 17). Here, an alternating input signal is used, and hysteresis loops of a ferroelectric material are obtained on an oscilloscope. The voltage applied across the ferroelectric sample appears across the horizontal plates of oscilloscope, thus plotting on the horizontal axis a quantity which is proportional to the electric field across the sample. The value of capacitance of sample material C_{sample} is chosen to be large enough so that most of the voltage drop occurs in the circuit across the ferroelectric material. The voltage V developed across the C_{sample} is proportional to the charge flowing through the ferroelectric materials (Sawyer and Tower, 1930; Stewart *et al.*, 1999). Thus, the polarization given by relation $P = q/A = (C_{sample})V/A$, where A is area of sample, is plotted on vertical axis. The variable capacitor C and resistor R as shown in Fig. 17 are used to compensate the phase factor introduced in the hysteresis loop due to the finite conductivity of the sample material.

Energy density properties

The parameters W_{str} , W_{rec} , W_{loss} and η are generally measured by calculating area in the P-E curve to study the energy storage capabilities of dielectric material. The relations for these parameters for a charging-discharging cycle are expressed in Eqs. 6, 7 and 8 (Jayakrishnan *et al.*, 2019b; Maraj *et al.*, 2019; Wang *et al.*, 2020; Zhang *et al.*, 2018). Fig. 7 mentions the shaded area in P-E loop representing the energy storage parameters for a dielectric material. The area under the P-E loop can be measured using data analysis and graphing software Origin from the P-E loop data.

The various steps followed to measure the area under the P-E loop curves are shown in Fig. 18. In the main window of software origin, choose 'Analysis' then 'Mathematics' and further 'Integrate' to calculate the area under the selected P-E curve. The calculated values of area are further used to measure the parameters W_{str} , W_{rec} , W_{loss} and η .

Polyvinylidene Fluoride (PVDF)

Introduction

The polyvinylidene fluoride (PVDF) is a fluoropolymer with the molecular formula $(-\text{CH}_2-\text{CF}_2-)_n$. The $-\text{CF}_2-$ and $-\text{CH}_2-$ groups in PVDF has a head ($-\text{CF}_2-$) to tail ($-\text{CH}_2-$) dominating configuration ($-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-$) with various molecular weight depending on number of molecular units in chain, distribution of molecular weight, the irregularity in chains, side chains, and crystalline regime. The strong ferroelectric properties in PVDF are closely correlated with its unique molecular structure (Kawai, 1969; Li and

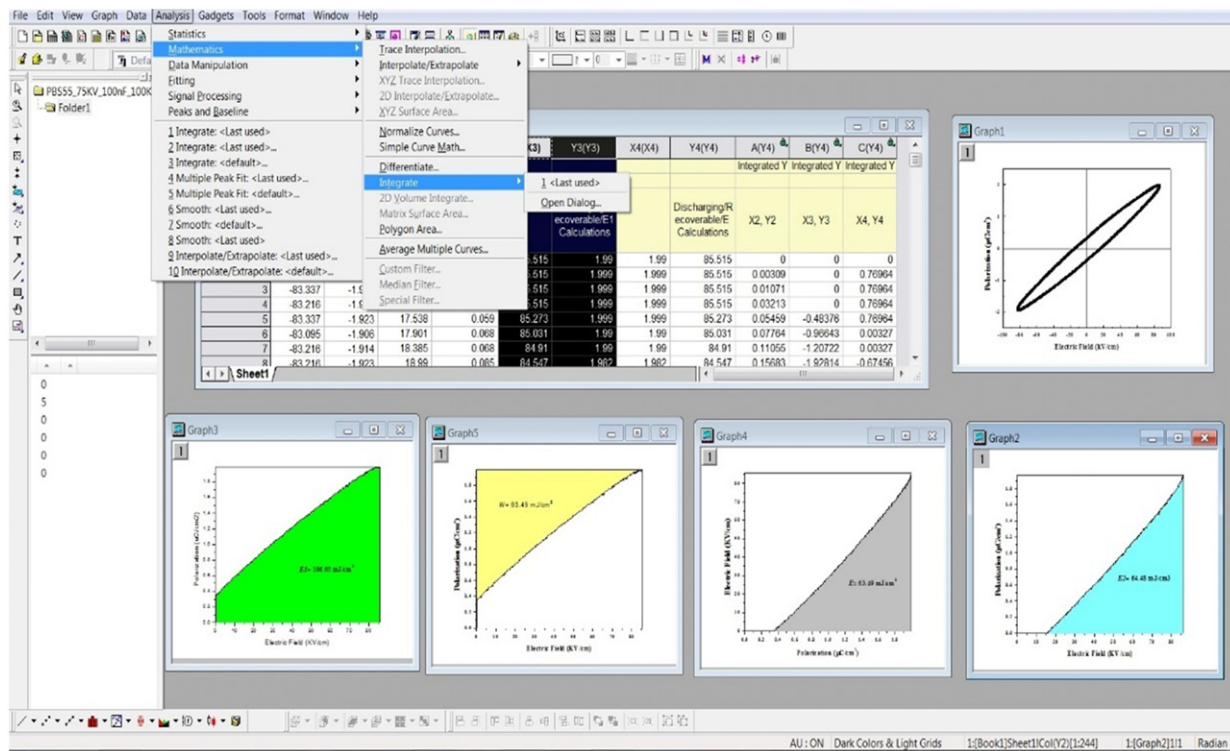


Fig. 18 Screenshot image of data analysis and graphing software “Origin” calculating the area under PE hysteresis loop curves to measure the storage energy density parameters.

Wang, 2016; Lovinger, 1983; Xia and Zhang, 2018). This observation has influenced the rapid advancements in ferroelectric polymer science. The polymer PVDF is said to be crystalline in nature because the vinylidene polymers possess no tactical issues associated with asymmetry in carbon and fluorine atoms and, due to its ability to easily pack into crystallographic lattices. However, due to presence of configurational head-to-head ($-\text{CF}_2\text{-CF}_2-$) or tail-to-tail ($-\text{CH}_2\text{-CH}_2-$) defects in PVDF, its crystalline fraction is limited to 50–60%. The C-F covalent bond is vital in fluoropolymers. Due to large difference in the electronegativity of carbon and fluorine atoms, the C-F bond in PVDF is highly polar. The magnitude of electric dipole moment of C-F bond is $6.4 \times 10^{-30} \text{ C m}$. The C-F bond with a strong dipole moment is an elementary unit of large electric polarization in PVDF. The different orientation of C-F bonds in different molecular conformations of PVDF affects its dielectric properties. The PVDF crystals are generated by the regular packing of molecular chains and, the packing configuration in which the internal moments are not canceled out generates the overall electric polarization. Moreover, the strong covalent C-F bond with bond energy 485 kJ/mol provides polymer PVDF the unique and characteristic mechanical, chemical, and electrical properties, excellent inertness to chemicals, hydrocarbons, acids, and alkali, chemical, aging, and weather resistance, excellent dielectric properties and so on (Chu *et al.*, 2006; Li and Wang, 2016; Lovinger, 1983; Ruan *et al.*, 2018; Xia and Zhang, 2018).

Other than the defects in the normal molecular chain configuration ($-\text{CF}_2\text{-CH}_2\text{-CF}_2\text{-CH}_2-$) in PVDF, it has five different polymorphs (α , β , γ , δ , and ϵ), including four known molecular chain conformations (α , β , γ , and δ) and a fifth (ϵ) suggested one (Fig. 19). The PVDF is generally available in a mixture of all types of known crystal phases in its crystalline region.

α -PVDF: It is the most common crystalline phase of PVDF. The molecular chain conformation in α -PVDF is trans-gauche-trans-gauche (TGTG). It is a combination of helical and planer zigzag formation. The helical structure is represented by a series of either G or TG. The unit cell parameters for α -phase packing are $a = 4.96 \text{ \AA}$, $b = 9.64 \text{ \AA}$, $c = 4.62 \text{ \AA}$, and $\alpha = \beta = \gamma = 90^\circ$ (Fig. 20). The one-unit cell in α -PVDF crystalline conformation possess no polarity due the packing of alternate chains with the component of their dipole moment normal to c-axis and anti-parallel to each other. Each TGTG' segment of the α -PVDF molecular chain possesses a net dipole moment but cancels due to anti-parallel packing configuration. Macroscopically, α -PVDF is non-polar due to self-cancellation of dipole moments (Li and Wang, 2016; Xia and Zhang, 2018). The α -PVDF is formed both during process of polymerization and by direct cooling from its melt state.

β -PVDF: The β -phase of PVDF is the most polar among all. It is the most attractive conformation due to the arrangement of molecules in all-trans conformation. It is the most extended planer zigzag fashion. The gauche-free molecular conformations in β -phase lead to a unique pseudo-hexagonal character of lattice which greatly facilitates the ferroelectric switching. The β -PVDF crystalline packing is in an orthorhombic unit cell with $a = 8.58 \text{ \AA}$, $b = 4.91 \text{ \AA}$, $c = 2.56 \text{ \AA}$ (Fig. 20). The PVDF β -phase is less favored than α -phase and is generally obtained by mechanical stretching of PVDF film near its melting point. The all-trans chain conformation positions all fluorine

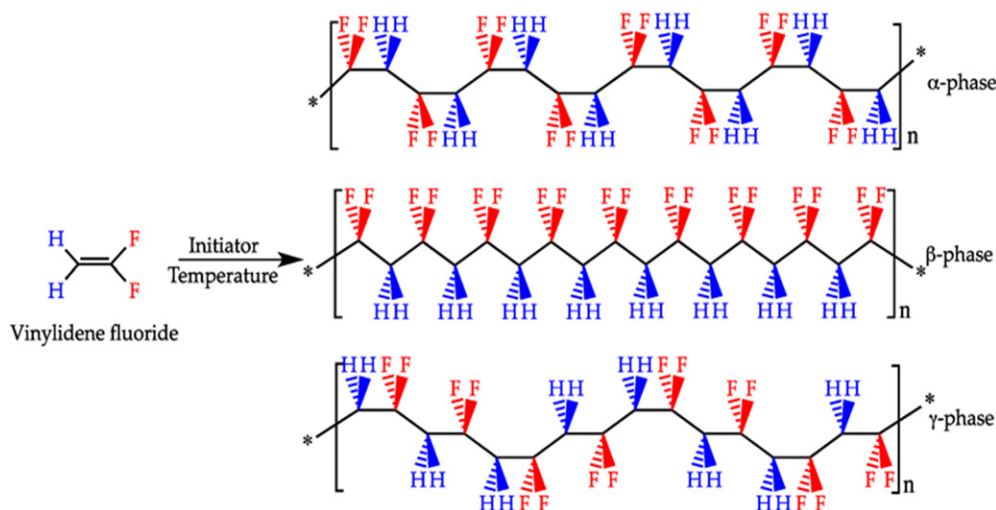


Fig. 19 Schematic chain conformations of different PVDF phases. Reprinted with permission from Ref. Cardoso, V., Correia, D., Ribeiro, C., Fernandes, M., Lanceros-Méndez, S., 2018. Fluorinated polymers as smart materials for advanced biomedical applications. *Polymers* 10 (161), 1–26.

atoms on one side and all hydrogen atoms on the other side of the chain which makes β -PVDF the most polar and electroactive among all (Li and Wang, 2016; Men *et al.*, 2019; Ruan *et al.*, 2018; Thakur *et al.*, 2016; Xia and Zhang, 2018).

γ -PVDF: The unit cell base with lattice parameter a or b in γ -phase of PVDF is similar to α -PVDF. The molecular conformation in γ -PVDF is TTTGTTTG' (T_3GT_3G'). The repeated length along c -axis in γ -PVDF (TTTGTTTG') is twice as that of α -phase (TGTG'). The PVDF in its γ -phase possesses a medium polarity. The PVDF in γ -phase is less usual and is obtained from ultra-high molecular weight PVDF.

δ -PVDF: In contrast to α -PVDF, the alternate chains in δ -phase the two are oriented in identical directions. Due to which δ -phase exhibit a net electric polarization. The δ -PVDF is polar macroscopically (Li *et al.*, 2013; Li and Wang, 2016; Xia and Zhang, 2018).

Processing of PVDF

The polyvinylidene fluoride (PVDF) is a semi-crystalline multiphase polymer (Kawai, 1969; Lovinger, 1983; Martins *et al.*, 2014; Ramadan *et al.*, 2014) which can be stabilized in its distinct polymorphs, α (TGTG', form II), β (TTTT, form I), γ (T_3GT_3G' , form III), δ and ϵ depending on the molecular chain conformation during the preparation of sample materials (Buonomenna *et al.*, 2007; Cai *et al.*, 2017; Cui *et al.*, 2015; Garg *et al.*, 2021; Hoque *et al.*, 2017; Li *et al.*, 2013; Liu *et al.*, 2011; Martins *et al.*, 2014). The crystalline phase stabilization and hence the properties of PVDF depends highly on the processing conditions during preparation of sample materials. The polymer PVDF and PVDF-based materials are generally processed by casting from melt and by cast from solutions with different solvents, techniques (Garg *et al.*, 2021). The different melting conditions and the solvents used further effects the stabilization process. Among all the molecular conformations in PVDF, TGTG' is the lowest energy conformation and the TGTG' conformation in α -PVDF is formed when PVDF is cooled directly from its molten state. The γ or β -phases of PVDF may produce by cooling from melt under high temperature or pressure conditions. In the casting of PVDF films from solutions, the type of stabilized crystalline phase varies with the solvent used. As an example, dimethylformamide DMF is the most common solvent used to synthesize PVDF film by solution-cast method. It mostly produces α or γ -phase in the PVDF film samples. The cyclohexanone as solvent was reported to produce mainly α and β -phases in PVDF. The highly polar solvents are reported to induce the polar phase formation in PVDF films. The evaporation rate of solvent also determines the fraction of a polar phase in PVDF sample.

The polar and non-polar molecular structural change in PVDF is a reversible phenomenon. The four different types of crystalline phases (α , β , γ , and δ) stabilized by PVDF processing either from melt or by solution casting are interconvertible when being post-processed thermally (high temperature annealing), mechanically (stretching) or electrically (electric poling) (Chu *et al.*, 2006; Martins *et al.*, 2014; Ruan *et al.*, 2018). The post-thermal treatment by annealing at high temperature promotes the conversion from α or δ -phases to γ -phase, and β -phase to α -phase in PVDF. The packing mode of molecular chains in each crystalline phase configuration possesses potential energy. The different in energy for each mode in PVDF is quite small that the heat energy during thermal treatment facilitates the movement of chains which triggers the conversion from one phase to another. The mechanical treatment by stretching of PVDF samples force the molecular chains into the most extended possible conformation leading to phase conversion. The stretching of α or γ -PVDF under optimized or controlled temperature conditions are likely to be converted into β -PVDF. The electric poling of PVDF samples in externally applied electric field influence the arrangement of molecular chains interacting with dipolar C-F bond or the polar segment of molecular chain. It is the elementary unit of polar nature of polymeric chains in PVDF. The α -PVDF converts to δ -PVDF in externally applied electric field which would convert to β -PVDF in further higher electric field. Fig. 21 depicts the different routes for mutual transformation of PVDF phases (Xia and Zhang, 2018).

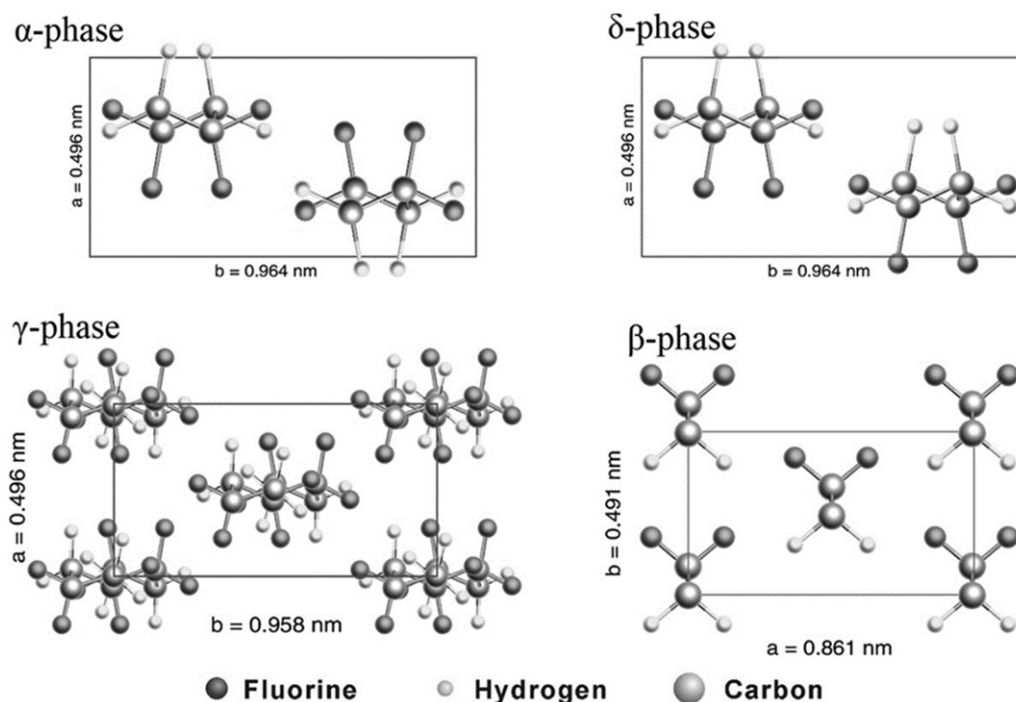


Fig. 20 Schematic view of the unit cells of the four crystalline phases of PVDF. Reprinted with permission from Ref. Li, Q., Wang, Q., 2016. Ferroelectric polymers and their energy-related applications. *Macromol. Chem. Phys.* 217, 1228–1244.

Applications of PVDF in Capacitive Energy Storage

Polyvinylidene fluoride (PVDF) and its co-polymers with a variety of unique mechanical, ferro/piezoelectric and pyroelectric properties are very attractive among many inorganic and organic material for wide range of applications (Gebrekrestos *et al.*, 2019). PVDF is a highly non-reactive and pure thermoplastic fluoropolymer because of the simple main chain chemical formula $(\text{CH}_2\text{-CF}_2)_n$ (Xia and Zhang, 2018). On electrical side, the different molecular conformations in PVDF have very different properties, for example the highly polar β -phase makes PVDF a unique ferroelectric material in the polymers, while the α -phase exhibit no ferroelectricity (Li and Wang, 2016; Xia and Zhang, 2018). The ferro/piezo/pyroelectric behavior in PVDF is closely related with the dielectric properties. The polymer PVDF due to its light weight and low density, low cost, flexibility, electrical/mechanical/thermal strength and ease of processing over the inorganic ceramic counterparts enjoys the numerous advantages in various applications (Li and Wang, 2016).

The relative permittivity ϵ_r and dielectric breakdown strength E_{BD} properties of dielectric materials affect their applicability in dielectric energy storage applications. PVDF, a ferroelectric polymer, have $\epsilon_r \approx 10$ at 120 Hz which is higher in comparison to the other non-polar polymers (Garg *et al.*, 2020). Its low dielectric constant value in comparison to inorganic ceramic counterparts limits its applicability in practical usage. However, due to its significant breakdown strength, the polymer PVDF is widely explored in ceramic-polymer composites for applications in dielectric energy storage capacitors (Garg *et al.*, 2020; Guo *et al.*, 2019; Li and Wang, 2016; Prateek *et al.*, 2016; Xia and Zhang, 2018).

Barium Calcium Zirconium Titanate (BCZT)

History of Piezoceramics

Piezoelectricity in certain solid materials is defined as an accumulation of electric charge when pressure was applied. It was observed in relation to crystallographic considerations with high instability of crystal structure (Wu, 2018). The formation of polar regions in crystal and their domain configuration also relates the piezoelectricity (Brown *et al.*, 1962; Wu, 2018). The sequential discovery and growth of piezoelectric materials lead to the better understanding of phenomenon. The evolution is a continuous process and among these continuous attempts the impact of some events or discoveries is so strong that they put their mark during history. The quartz, Rochelle salt, barium titanate BaTiO_3 , BT, lead zirconium titanate $\text{Pb}(\text{Zr,Ti})\text{O}_3$, PZT, lithium niobite/tantalate, relaxor ferroelectrics, PVDF, lead-free piezoelectrics, and composite materials are the solid material which endure the benchmarks in a sequence in the history of piezoelectricity (Eubank *et al.*, 1952; Hong *et al.*, 2016). In 1880, piezoelectricity was first demonstrated in naturally occurring single-crystal quartz taking crystallographic considerations as a unique feature of certain crystals which lack inversion symmetry. The discovery of piezoelectricity in BT polycrystalline ceramic in 1940 s was a breakthrough in the fact that the ceramic materials where random orientation is unavoidable can have high piezoelectricity of practical

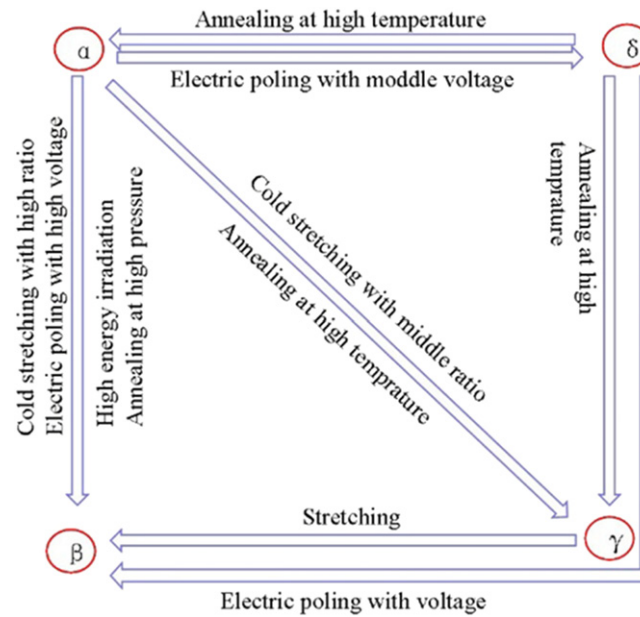


Fig. 21 Mutual transformation routes and preparation methods of different PVDF. Reprinted with permission from Ref. Xia, W., Zhang, Z., 2018. PVDF-based dielectric polymers and their applications in electronic materials. *IET Nanodielectr.* 1, 17–31.

importance and inspired for the search and development of new ceramic materials having enhanced piezoelectric properties (Jaffe, 1958). This led to discovery of PZT ($Pb(Zr_xTi_{1-x})O_3$) piezoelectric ceramic system in 1950s which is still the most widely used and studied piezoceramic due to its excellent properties. For PZT, the maximum piezoelectric properties were observed when the composition approached a phase boundary between rhombohedral and tetragonal crystal symmetry i.e. in PZT composition the rhombohedral and tetragonal crystal symmetry was found to coexist at room temperature (Jaffe *et al.*, 1954). The discovery of PZT was a turning point, not only because of its excellent properties but also because it introduced the scientific community with the new concept of phase boundaries. After this, the existence of phase boundaries in piezoceramic composition is thought to be key to get the highest output (Cao and Cross, 1993; Megaw, 1952). Many piezoelectric systems such as, PZT-PT ($Pb(Zn_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$) and PMN-PT ($Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$) are widely studied due to their outstanding properties for applications in sensors, actuators and so on (Panda, 2009; Shrout and Zhang, 2007). During last decade due to the environmental concerns of toxic-lead (Pb), many lead-free systems such as sodium-potassium niobates KNN ($(K,Na)NbO_3$), barium calcium zirconium titanate BZT-BCT ($Ba(Ti_xZr_{1-x})O_3$ - $(Ba_xCa_{1-x})TiO_3$) and, various secondary and ternary systems of bismuth ferrite BFO [$BiFeO_3$] e.g., BFO-BTO ($BiFeO_3$ - $BaTiO_3$), BFO-BTO-BG ($BiFeO_3$ - $BaTiO_3$ - $BiGaO_3$), BFO-BTO-BZT ($BiFeO_3$ - $BaTiO_3$ - $Bi(Zn_{0.5}Ti_{0.5})O_3$) are widely explored (Liu and Ren, 2009; Wu *et al.*, 2016). Table 1 summarizes the history, recent work done and comparison of few piezoelectric systems.

Relaxor Ferroelectrics

The compositional modifications in piezoceramics to optimize the existence of phase boundaries at room temperature is the most explored technique to get the outputs of practical importance. The chemical substitution or doping of ions with different polarizabilities, valence state and size at different sites of crystal structure (ABO_3 perovskite) produce sufficient dipolar defects in crystal. It creates high degree crystalline disorder. The disordered crystal breaks the translational symmetry and prevents the formation of long-range order. This results into the formation of polar nanoregions PNRs (Eremenko *et al.*, 2019; MacUtkevicius *et al.*, 2011; Shvartsman *et al.*, 2005; Viehland *et al.*, 1998). The difference in ionic radius, electronegativity and valence state in the A- and B-site can induce enough charge fluctuation, vacancies and local ordering to introduce the relaxor property (Chu *et al.*, 1993; Liu *et al.*, 2018). The relaxor properties due to the formation of PNRs in crystal can be characterized by its slim ferroelectric P-E hysteresis loop. The compositional disorder in the crystal lattice with disorder in the arrangement of different ions on the crystallographic sites is the common feature of relaxors. Relaxor ferroelectrics includes a large group of oxides solid solutions, with a perovskite structure (de Mathan *et al.*, 1991; Guo *et al.*, 1990; Kleemann, 2006; Randall and Bhalla, 1990; Samara, 2003). The existence of lattice disorder and PNRs appear to be the two essential ingredients for the occurrence of relaxor behavior in perovskites (Gupta and Viehland, 1999). The existence of PNRs was evidenced by TEM (Randall and Bhalla, 1990), neutron diffraction and diffuse X-ray scattering studies (de Mathan *et al.*, 1991). The charge and structural inhomogeneities generated in the crystal structure of barium titanate due to Ca and Zr ions doping lead to formation of polar nanoregions in BCZT crystal which results in its relaxor-type ferroelectric properties (Jayakrishnan *et al.*, 2019b; Maraj *et al.*, 2019; Peddigari *et al.*, 2018; Shvartsman and Lupascu, 2012).

Table 1 A tabular summary of history, recent work done and comparison of few piezoelectric systems with material/system name, year, origin of piezoelectricity, piezoelectric coefficient d_{33} value and Curie temperature T_C .

Material/System	Year	Origin of enhanced piezoelectricity	d_{33} value (in pC/N)	T_C (in °C)
Quartz crystal	1880	–	–	–
Rochelle salt Sodium potassium tartrate $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4 \text{H}_2\text{O}$		Hydrogen bonds		– 18 & 24
Potassium dihydrogen phosphase KH_2PO_4 (<i>KDP</i>)	1935	Hydrogen bonds		
Electrically poled BaTiO_3 (<i>BTO</i>)	1947	PPT (R-O, O-T, T-C)	190	120–135
LiNbO_3 (<i>LN</i>) LiTaO_3 (<i>LT</i>)	1949	–	–	1140
$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (<i>PZT</i>)	1950	MPB (R-T)	200–750	600
BiFeO_3 (<i>BFO</i>)	1957	–	50	180–320
$(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - BaTiO_3 (<i>BNT-BTO</i>)	1961	MPB (R-T)	125	> 700
PVDF	1969	–	6–7	320
PZT-PVDF composites	1972	–	–	–
$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (<i>PZT-PT</i>) $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (<i>PMN-PT</i>)	1997	Polarization rotation	2500	–
$(\text{K},\text{Na})\text{NbO}_3$ (<i>KNM</i>)	Last 10–15 years	MPB (R-O, O-T, R-T) PPB (R-O, O-T, T-C)	–	–
$(\text{K},\text{Na})(\text{Nb},\text{Sb})\text{O}_3$ - BaZrO_3 -(Bi,K) HfO_3 (<i>KNNS-BZ-BKH</i>)	2016	MPB (R-T)	570	–
$(\text{Li},\text{Na},\text{K})\text{NbO}_3$ - BaZrO_3 -(Bi,Na) TiO_3 (<i>LKNN-BZ-BNT</i>)	2017	Diffused phase boundaries	330 (<10%) (25–100 °C) 380 (<20%) (25–200 °C)	> 260
$\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ -($\text{Ba}_{0.7}\text{Ca}_{0.3}$) TiO_3 (<i>BZT-BCT</i> , <i>BCZT</i>)	Last 10–15 years	Tilted MPB PPB (R-T, T-C)	620	93
$\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ -($\text{Ba}_{0.7}\text{Ca}_{0.3}$) TiO_3 (<i>BZT-BCT</i>) Nanowires	2017	Tilted MPB PPB (R-T, T-C)	35pV^{-1}	300
BiFeO_3 - BaTiO_3 (<i>BFO-BTO</i>)	Last 10–15 years	MPB (R-T)	240	456
BiFeO_3 - BaTiO_3 - BiGaO_3 (<i>BFO-BTO-BG</i>)	2015	MPB (R-T)	402	454
BiFeO_3 - BaTiO_3 - $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (<i>BFO-BTO-BZT</i>)	2015	MPB (R-T)	324	466
PVDF-BCZT Composites	–	–	–	–

The properties and physics of relaxor behavior in ferroelectrics are very different from those of normal ferroelectrics. The ferroelectric PE hysteresis loop is a significant feature of ferroelectric materials. At low temperature ferroelectric-phase in normal ferroelectrics, the large value of remnant polarization P_r is due to the cooperative nature of ferroelectric phenomenon. The maximum polarization and remnant polarization in normal ferroelectrics decrease with increase in temperature and at T_c vanishes completely. However, in relaxor-ferroelectrics, the large polarization is due to the orientation of nano domains in PNRs with electric field (at sufficiently high value) which re-acquire their random orientations on removing the field. It results in a slim ferroelectric PE hysteresis loop, a characteristic feature of relaxor-ferroelectrics. With increase in temperature, the magnitude of polarization in relaxors decreases smoothly through T_m and retains finite value even at higher temperatures (Samara, 2003).

Crystal Structure and Properties of Barium Calcium Zirconium Titanate (BCZT)

Transition metal oxides

An element in the periodic table having partially filled d-shell or which forms cation with incomplete d-shell is called transition metal. Iron *Fe*, cobalt *Co*, nickel *Ni*, titanium *Ti*, zirconium *Zr* etc. are the transition elements belonging to different d-block series of the periodic table. Transition metal-based oxides are one of most extensively explored inorganic solids which offer a significant range of chemical and physical attributes. The remarkable features of these materials originate due to the distinctive nature of outer d-electrons which give rise to multiple oxidation states to the cations. These materials also show variation from ionic to metallic character in the nature of their metal-oxygen bonds (Rao, 1989). The crystal structure of the transition metal oxides strongly affects their electric properties i.e., show strong structure-properties coupling. The perovskite, spinel and pyrochlore are the different types of crystal structure forms. The transition metal oxides display structural changes by altering the pressure, temperature, chemical composition and, hence the properties can traverse from one to another zone. Transition metal oxides showcase properties in wide range of material classes like high temperature superconductivity, colossal magnetoresistance CMR, ferro/piezoelectricity, relaxor ferroelectrics, multiferroics (Cava et al., 1987; Cohen, 1992; Dong and Liu, 2012; von Helmolt et al., 1993; Jin et al., 1994).

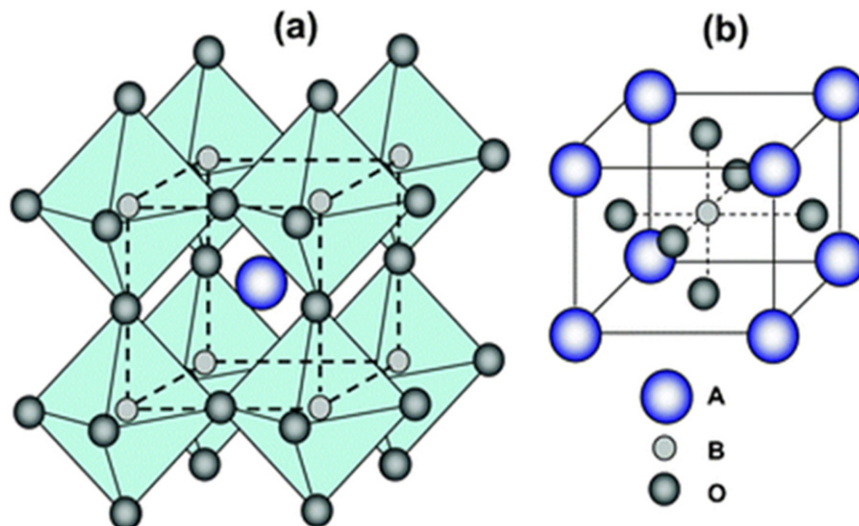


Fig. 22 Typical perovskite structure. Reprinted with permission from Refs. Sarfraz, A., Raza, A.H., Mirzaeian, M., Abbas, Q., Raza, R., 2020. Electrode materials for fuel cells. Reference Module in Materials Science and Materials Engineering. Elsevier. pp. 1–16. West, A.R., 2006. Inorganic functional materials: optimization of properties by structural and compositional control. Chem. Rec. 6, 206–216.

Perovskite structure

Among all the possible crystal structures for transition metals based oxides, the perovskite-type structured oxide crystals are the most explored and, reported to have the best piezoelectric and ferroelectric properties. These are generally represented by chemical formula ABO_3 , where A and B represents the two different sites for cation atoms. The ferroelectrics, relaxor-ferroelectric, piezoelectric and multiferroic materials with perovskite-type crystal structure are being widely studied. The perovskite structure is advantageous due to the many different cations with variable polarizabilities, valence state and size can be substituted on different sites without affecting the overall crystal structure drastically. The possibility of substitution or doping of different cations and in different proportions could help in achieving the complete solid solution over the wide range of composition (Eric Cross, 1987). The anisotropy in crystal structure and charge density distribution for the relaxor-ferroelectric and piezoelectric properties is large in perovskites among all the structures. The phase transitions can readily happen in perovskites and, modifications in the sequence of phase transitions induced by structural changes due to chemical modifications are easy. The perovskite crystal structure is similar to that of mineral perovskite ($CaTiO_3$), which is orthorhombic (Qin *et al.*, 2000). The perovskites are centrosymmetric ideally with general formula ABO_3 . The valency of cation at 'A' site generally varies from + 1 to + 3 while at 'B' site it is + 3, + 4 or + 5. Fig. 22 shows the schematic representation of ABO_3 type perovskite. The body center position of the unit cell is occupied by the cation at B-site while the A-site cations are at the corner position of cube. The oxygen atoms are at the face centered position. An octahedron is formed by the oxygen atoms around the B-site cation.

The properties of ABO_3 perovskite oxides are dependent on the nature of on cations present on its A and B lattice sites. The ions of alkaline (e.g., sodium *Na*), alkaline earth (e.g., calcium *Ca* and barium *Ba*) and lanthanides (e.g., lanthanum *La*) preferably occupies A-sites whereas B-site cations mainly comprises of ions of transition metals (Peña and Fierro, 2001). In chemical substitution or modification process in perovskites, when a cation at A-site is replaced partly by a cation having lower oxidation state, then the neutrality of electric charge in the compound is achieved either by creation of oxygen vacancies or increase in the oxidation state of B-site cations. Subsequently, substituting a cation of higher oxidation state either hinders the formation of oxygen vacancies or decrease the oxidation state of cation at B-site. The oxygen ion movement gets facilitated due to presence of oxygen vacancies, and as a result the oxygen based ionic conductivity of the perovskite oxide are affected (Cherry *et al.*, 1995; Warren *et al.*, 1996). The electronic conduction becomes viable due to electron hopping between the metal ions with variable valance state at the B-site.

Similar to the charge neutrality constraints, the size constraint factor is important to get a stabilized crystal structure. The size constraint factor is described by the tolerance factor $\mathcal{T}$ (Sixl, 1991).

The tolerance factor $\mathcal{T}$ for a perovskite structure is

$$\mathcal{T} = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (19)$$

where; r_A , r_B and r_O are the radius of A-site cation (in 12 coordination), B-site cation (in 6 coordination) and oxygen ion respectively.

For an ideal perovskites, the value of ' $\mathcal{T}$ ' should be in the range of 0.95–1.04 for cubic symmetry. It is larger for the distorted perovskite crystal structure (Shannon, 1976).

Many perovskites exhibit other crystal structures like rhombohedral, tetragonal, trigonal or orthorhombic with change in A and B atomic species. This substitution result in the change of $\mathbb{T}$ value due to different ionic radii, which in turn indicates lowering of crystallographic symmetry and giving way to other crystal structures. Hence, the changes in molecular formula and crystal structures symmetry could tailor a wide range of properties. Doping at A or B site with aliovalent cation creates mixed valance and with different sized cation may alter the structure. So the substituted compounds display different properties from their parents and may give rise to new features like CMR and the modifications of the magnetic properties (Blasco *et al.*, 1996; von Helmolt *et al.*, 1993; Jin *et al.*, 1994).

Crystal Structure of Bczt

Barium titanate BT is a transition metal-based oxide perovskite which is one of most extensively explored inorganic solids, offering a significant range of chemical and physical attributes. In the cubic unit cell of barium titanate, Ba^{2+} ions exist at the corners, Ti^{4+} lies in the center of cell and O^{2-} occupying the face center. demonstrate the crystal structure of BT (Villafuerte-Castrejón *et al.*, 2016). In the typical perovskite structure as shown in Fig. 22, for barium titanate A and B represents the Ba and Ti respectively (Maraj *et al.*, 2019). Barium titanate BaTiO_3 , BT is the polycrystalline ferroelectric ceramic in which the phenomenon of piezoelectricity was first discovered.

Barium titanate (BT), generally, undergoes structural phase transitions with temperature as; ferroelectric rhombohedral (R) $T_{R-O} \approx -90^\circ\text{C}$ ferroelectric orthorhombic (O) $T_{O-T} \approx 0^\circ\text{C}$ Ferroelectric Tetragonal (T) $T_C \approx 125^\circ\text{C}$ Paraelectric Cubic (C) (Devonshire, 1949; Tian *et al.*, 2012; Villafuerte-Castrejón *et al.*, 2016). To study the phase boundaries induced enhancement in piezoelectric and dielectric properties of BT, different dopants at A and B-site of BT (where, typically, A = Ca, Sr, La; B = Nb, Ta, Zr) are used (Batoo *et al.*, 2021; Juneja *et al.*, 2010; Kumar *et al.*, 2011; Verma *et al.*, 2021a; Zhou *et al.*, 2016). Especially Ca and Zr ions doping, are of great interest due to a high d_{33} value of ≈ 600 pC/N has been reported in one of the BCZT compositions (Liu and Ren, 2009; Villafuerte-Castrejón *et al.*, 2016). With Ca-doping at Ba-site, T_{R-O} and T_{O-T} shift towards lower temperature while T_C moves slightly up and shifting of transition temperatures increase with an increase in doped-Ca content (Mitsui and Westphal, 1961). However, with an increase in the content of doped-Zr at Ti-site, T_{R-O} and T_{O-T} shifts towards higher temperature and T_C moves down i.e., three phase transition points move closer to each other (Henning *et al.*, 1982). The various compositions of BCZT, $[\text{z}((\text{Ba}_x\text{Ca}_{1-x})\text{TiO}_3)-(z-1)(\text{Ba}(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3)]$ have their own pattern of phase transitions depending on the x, y and z values. The synthesis technique, processing temperature, sintering process and temperature are the factors that further affect the phase transitions and, structural, morphological and dielectric properties of nanomaterials in general (Gao *et al.*, 2017; Mohanty *et al.*, 2019a; Tian *et al.*, 2012; Verma *et al.*, 2021b; Villafuerte-Castrejón *et al.*, 2016). Barium calcium zirconium titanate $[(x-1)(\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3)-x((\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3)]$ (xBZT-(x-1)BCT) is a lead-free piezoceramic which has the particularity of having a high value of d_{33} compared to other piezoelectrics without lead. This system has a phase limited morphotropic phase boundaries MPBs similar to that of the PZT near its composition $x = 0.5$ (Liu and Ren, 2009; Tian *et al.*, 2012). The Fig. 23 shows the phase diagram of this system.

In this phase diagram (Fig. 23), the MPB separates the rhombohedral ferroelectric phase (BZT side) from tetragonal phase (BCT side). The basic method to achieve highly ferro/piezoelectric materials is to position the composition of system in the vicinity of structural phase transition between the different ferroelectric phases. The instability in polarization state caused by crystalline instability during phase transition allows the easy rotation of polarization direction under the influence of applied electric field. It results in high permittivity and ferro/piezoelectric properties, and relaxor-type ferroelectric behavior which is characterized by slim P-E hysteresis loop.

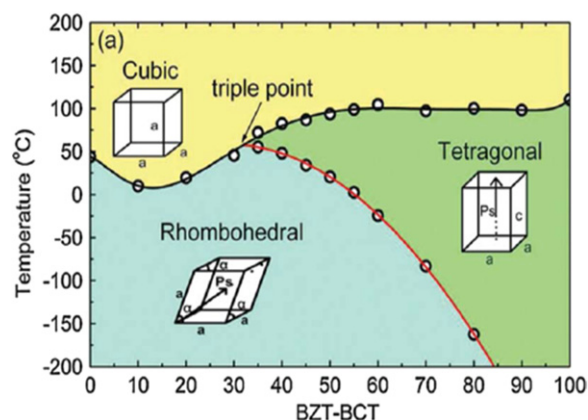


Fig. 23 BZT-BCT system phase diagram. Reprinted with permission from Refs. Liu, W., Ren, X., 2009. Large piezoelectric effect in Pb-Free ceramics. *Phys. Rev. Lett.* 103, 257602. (1–4). Panda, P.K., Sahoo, B., 2015. PZT to lead free piezo ceramics: A review. *Ferroelectrics* 474, 128–143.

Application of BCZT in Capacitive Energy Storage

The lead-free BCZT in the composition $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ for $x = 0.5$ has been found to have excellent ferro/piezoelectric properties comparable to well-known PZT piezoceramics owing to their morphotropic phase boundary (MPB) (Liu and Ren, 2009). Furthermore, BCZT $(1-x)\text{BCT}-x\text{BZT}$ due to its relaxor-type ferroelectric behavior was explored with $x = 0.1-0.2$ for capacitive energy storage and, the W_{rec} of 0.68 J cm^{-3} at an applied field of 170 kV cm^{-1} was achieved in $0.85\text{BZT}-0.15\text{BCT}$ composition (Puli *et al.*, 2011). Since then, the various compositions of BCZT and its doped-form has been thoroughly investigated to achieve ultrahigh energy density properties. Jayakrishnan *et al.* (2019a) have studied the compositions $(1-x)\text{BCT}-x\text{BZT}$ for $x = 0.4-0.6$ that lies in MPB for their energy storage performance and obtained an energy density of 149 mJ cm^{-3} at 35 kV cm^{-1} at $x = 0.6$ (Jayakrishnan *et al.*, 2019b). Further, they investigated the doping or inclusion of paraelectric SrTiO_3 in $(1-x)[0.6\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.4(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]-x[\text{SrTiO}_3]$ (BZCT) ceramics in order to improve ΔP and consequently enhance the W_{rec} and η values (Jayakrishnan *et al.*, 2019a). The atomic radii of Sr ($R_{\text{Sr}} = 1.16 \text{ \AA}$) ion is smaller than Ba ($R_{\text{Ba}} = 1.35 \text{ \AA}$). The SrTiO_3 doping in BCZT ceramics replaces Ba-ions with Sr-ions at A-site. The lattice parameters, cell volume and tetragonal distortion of unit cell decreases with increase in x-value or Sr-ion content due to its smaller atomic radii. The incorporation of STO in BCZT ceramics weakened their polar nature and reduced spontaneous polarization leading to increase in ΔP and hence improve W_{rec} and η values. In this work, BCZT-STO ceramics in composition $0.85\text{BZCT}-0.15\text{STO}$ is optimized to possess W_{rec} of 0.987 J cm^{-3} with $\eta \approx 84\%$ at an electric field of 108 kV cm^{-1} , which is higher than as reported earlier in BZCT ceramic-based capacitors. In the most recent work, A. R. Jayakrishnan *et al.* (2021) has reported the novel strategy to the energy storage performance by enhancing ΔP and E_{BD} simultaneously in BCZT ceramics (Jayakrishnan *et al.*, 2021). The distribution of ZnO at the grain boundaries of BCZT in ZnO/BCZT semiconductor/relaxor composites helped in reducing the formation of discharge streamers leading to enhanced E_{BD} in BCZT ceramics. Moreover, ZnO doping induced pseudocubic BCZT structural phase stabilization i.e., decrease in unit cell distortion which improved the ΔP value. The energy storage properties of BZCT/ZnO ceramic composites having 1 wt% ZnO content is optimized with W_{rec} of 2.61 J cm^{-3} and η of 74.2%, at an electric field of 282 kV cm^{-1} . Doping, microstructure control, domain engineering, multi-layered structures, mixing ferroelectrics with paraelectrics and semiconductors, and novel processing approaches are the different strategies to improve the relaxor behavior and energy storage performance in ferroelectrics (Jayakrishnan *et al.*, 2021; Jayakrishnan *et al.*, 2019a; Liu *et al.*, 2022; Munir *et al.*, 2021; Silva *et al.*, 2019; Veerapandian *et al.*, 2020).

PVDF/BCZT Ferroelectric Polymer-Nanocomposites

Introduction

The ever increasing requirement of variety of material-form exhibiting distinct characteristics/properties, with the continuous progress in the field of electric industries and modern electronics, is difficult to meet with single phase polymeric or ceramic materials (Lu *et al.*, 2017). For the improvement of dielectric properties in polymers, in this regard, the highly functional organic, ceramic and carbon-based fillers or dopants are randomly dispersed in the polymer matrix (Amiri and Rahimi, 2016; Lu *et al.*, 2017; Luo *et al.*, 2019; Men *et al.*, 2019; Patra *et al.*, 2018; Shepelin *et al.*, 2019; Thakur *et al.*, 2018). The nanofillers with large surface area provide an active size for effective polymer phase and dielectric properties modulation (Li *et al.*, 2014; Martins *et al.*, 2014). The inorganic ceramic particles dispersed in the polymer matrix not only improve the dielectric properties of polymers but also contribute as a functional phase widening the range of applications of polymer-nanocomposites. In past, various inorganic dielectric ceramics and polymers have been explored and optimized to get the outstanding properties at an individual level (Hong *et al.*, 2016; Koruza *et al.*, 2018; Yang *et al.*, 2015). The hybrid system (i.e., mixing different materials for their emerging and exciting new properties) is a concept which rather focuses more on the aspects of practical requirements at the cost of best from its different elements (de Oliveira Sousa Neto *et al.*, 2017; Nicole *et al.*, 2014). For the purpose of piezoelectricity-based energy harvesting applications, the various flexible lead-based systems either involving electroactive thin-film deposited on a flexible substrate or an electroactive ceramic embedded in the flexible polymer matrix were reported in past (Hwang *et al.*, 2016; Jain *et al.*, 2015; Li *et al.*, 2017; Mishra *et al.*, 2019). Combining PVDF and BCZT as polymer-nanocomposites integrates the ferro/piezoelectric properties of BCZT nanoceramics with flexibility of PVDF polymer through proper synthesis technique to make a suitable flexible-electroactive material form for applications in piezoelectricity-based energy harvesting and dielectric energy storage devices (Chen *et al.*, 2017; Hoque *et al.*, 2017; Stadlober *et al.*, 2019). Hence, in PVDF/BCZT hybrid composite systems, the ferroelectric PVDF as polymer matrix provides mechanical, thermal and charge-discharge cyclic stability, flexibility and, good mechanical and chemical stability properties to the composite whereas the BCZT ceramic contributes as a major functional phase to the composite.

In semi-crystalline PVDF polymer, polarization involves the orientation of polar phases and accumulation of space charge (SC) between the crystalline and amorphous phase (Chu *et al.*, 2006). The incorporation of BCZT particles in the PVDF matrix will modulate the polymer phase stabilization. Also, BCZT will add strong polarity groups derived from ionic polarization in its cell structure to polymer and, also increase the SC accumulation at the interface of ceramic and polymer (Lewis, 2005; Luo *et al.*, 2019; Maraj *et al.*, 2019; Zhang *et al.*, 2018). These variations in the inner charge environment of PVDF will affect the overall polarization mechanism and hence, improve the dielectric properties. The ferroelectric ceramic-polymer composites are investigated thoroughly, both to increase the dielectric constant of a polymer matrix and to increase the breakdown strength of ceramics for energy

storage capacitors (Prateek *et al.*, 2016). The significantly enhanced dielectric constant and energy storage density found in PVDF/BCZT composites which make them the most suitable candidates for applications in energy storage devices (Fu *et al.*, 2015; Lu *et al.*, 2017; Valiyaneerilakkal *et al.*, 2017; Wang *et al.*, 2017; Wang *et al.*, 2020; Zhang *et al.*, 2018).

Various Factors Affecting its Properties

The BCZT nanoparticles shape and size, PVDF phase stabilization, PVDF/BCZT wt% and the ceramic-polymer interfacial interactions are the factors which affect the overall electrical properties of PVDF/BCZT polymer-nanocomposites (Hu *et al.*, 2020). The processing technique affecting the degree of mixing and morphology of sample materials is another factor controlling or affecting the overall dielectric properties of composites. The idea behind the polymer-nanocomposites is the inclusion of modest amount of ceramic nanofillers having enhanced electronic functional properties into polymer matrix through proper synthesis technique including modifications for homogeneous distribution of nanofillers and strong interfacial interactions to optimize or achieve the most suitable material-form for different applications (Chandra Pandey *et al.*, 2021). Apart from the chemical, thermal and mechanical stability, and flexibility properties of polymers, the electroactive polymers also contribute their part in the overall functional properties of polymer-nanocomposites.

Applications in Capacitive Energy Storage

The energy density properties in dielectrics require high ϵ_r and E_{BD} , and relaxor-type ferroelectric behavior which is generally characterized by slim-hysteresis loop. High ϵ_r and E_{BD} values lead to high W_{st} however the slim ferroelectric loop is required to have low W_{loss} achieving high W_{rec} and η . High ϵ_r and E_{BD} can't be simultaneously due the underlying physics behind it. Hence, dispersion of ceramic nanoparticles of high permittivity in polymer matrix having high breakdown strength is an approach to enhance ϵ_r and E_{BD} concomitantly. The ferroelectric PVDF/BCZT nanocomposites have been widely explored and studied for their energy density capabilities in capacitive energy storage. While comparing the energy storage density of PVDF/BCZT composites as reported in literature, the applied electric field is an important factor to consider. Lu *et al.* (2017) reported that the PVDF/BCZT composites exhibits the maximum energy density of 3.69 J cm^{-3} for 20 vol% of BCZT doping which was about 2.3 times as compared to 1.66 J cm^{-3} value for pure PVDF sample when the applied field while taking measurements was 125 kV mm^{-1} (i.e., 1250 kV cm^{-1}) (Lu *et al.*, 2017). Adireddy *et al.* (2015) fabricated the composite films of barium titanate (BT), barium calcium titanate (BCT) and barium zirconium titanate (BZT) fillers in PVDF polymer matrix, and reported the maximum energy density of 7.74 J cm^{-3} at an applied field of about 2 MV cm^{-1} (i.e., 2000 kV cm^{-1}) (Adireddy *et al.*, 2015). In our work, we reported the maximum stored energy density of 70.46 mJ cm^{-3} in PVDF/BCZT nanocomposite film at an applied field of about 80 kV cm^{-1} for 50 wt% BCZT content composition. In composites, the dispersed nanoparticles in polymer matrix often lead to agglomeration or formation of ceramic clusters due to their high surface energy. It results in separation of ceramic phase from the polymer. And hence, formation of inhomogeneous film which degrades the overall dielectric properties of composites (Patra *et al.*, 2018). The ceramic nanoparticles with surface modifications are extensively investigated to improve the interfacial interactions between the ceramic and polymer matrix (two different material phases) and, for homogeneous and uniform dispersion of ceramic particles (Zhang *et al.*, 2016). Fu *et al.* (2015) modified the surface of barium titanate (BT) particles by water-soluble polyvinylpyrrolidone (PVP) and reported the improvement in results for composites with surface-modified BT particles as compared to unmodified filler particles. It reported the maximum energy density of composite with 40 vol% modified-BT particles to be 30 mJ cm^{-3} at 10 kV mm^{-1} (i.e., 100 kV cm^{-1}) (Fu *et al.*, 2015). Patra *et al.* (2018) showed the improved dielectric and ferroelectric properties in PVP surface-modified BCZT composites in PVDF matrix (Patra *et al.*, 2018). Luo *et al.* (2019) investigated the BCT-BZT surface modifications with dopamine in epoxy resin composites (Luo *et al.*, 2019). The dielectric constant and the energy storage density of ceramic-polymer composites depend on the uniform and homogeneous dispersion of ceramic particles in the polymer matrix, and the interfacial interactions between the ceramic and polymer phases in composites (Pan *et al.*, 2017). The selection and usage of appropriate surface modifier is a key factor in enhancing the overall dielectric properties in composites.

Future Scope and Discussions

To achieve the desired ϵ_r , E_{BD} and energy density properties in polymer-nanocomposites requires optimizing physical parameters of nanofillers, wt% of nanofillers, homogeneous distribution of nanofillers and nanofiller-polymer interface characteristics. The increase in nanofiller wt% improves the electrical properties of polymer-nanocomposites but up to a certain limit only. The overloading of nanofillers in polymer matrix lead to decrease in electrical properties due to agglomeration and overlapping of filler particles leading to reduction in interfacial and space charge polarizations. The agglomeration of nanofillers also leads to inhomogeneous field distribution in composites which deteriorates its breakdown strength. A machine learning (ML) driven approach in the process of designing polymer-nanocomposites for desired properties, also showed that the effect of nanofiller permittivity and bandgap on E_{BD} and ϵ_r of nanocomposites follow the opposite trend i.e., it is difficult to improve ϵ_r and E_{BD} simultaneously choosing any type of nanofiller. In a approach towards better ferroelectric polymer-nanocomposites techniques involving to tailor the shape and size of nanofillers, their orientation and distribution in matrix, and nanofiller-polymer interfacial bonding are important to improve the trade-off between ϵ_r and E_{BD} in polymer nanocomposites (Hu *et al.*, 2020; Tawade *et al.*, 2021; Zhang *et al.*, 2019; Zhu *et al.*, 2021).

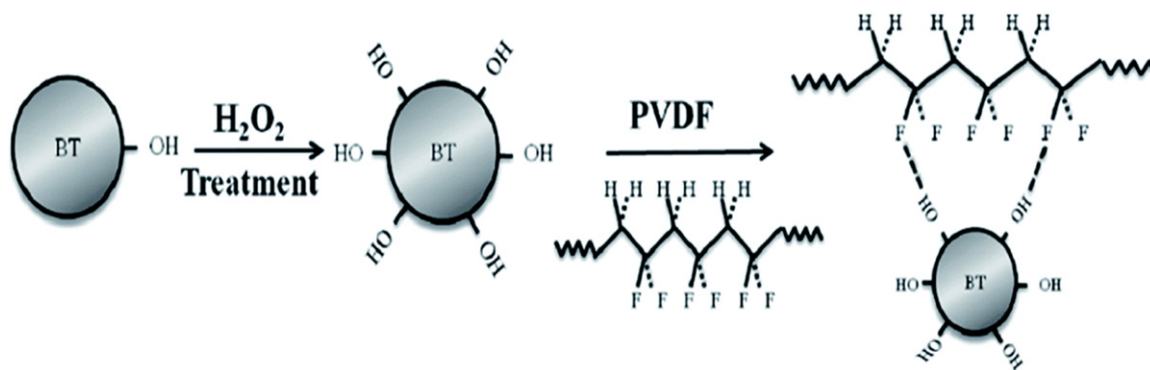


Fig. 24 Schematic diagram of hydroxylation of BT particles and formation of hydrogen bond in hydroxylated BT/PVDF nanocomposites. Reprinted with permission from Ref. Zhou, T., Zha, J.W., Cui, R.Y., *et al.*, 2011. Improving dielectric properties of BaTiO₃/ferroelectric polymer composites by employing surface hydroxylated BaTiO₃ nanoparticles. *ACS Appl. Mater. Interfaces* 3, 2184–2188.

Shape and Size of Nanofillers

The ϵ_r of polymer-nanocomposites can't be improved simply by increasing wt% of nanofillers of high permittivity in polymer matrix. The excessive nanofiller deteriorate the overall properties of composites. In this regard, the strain engineering in ferroelectrics involving nanostructuring (i.e., optimizing particle size and shape) provides a new route to tailor the desired properties. The chemical-solution-derived (CSD) synthesis techniques offer a cost-effective and friendlier approach for strain-tuning in ferroelectric systems to widen their current applicability (Zhang *et al.*, 2020). Nanostructures with large surface area provide an active size for effective modulation in properties (Li *et al.*, 2014; Martins *et al.*, 2014). Datta *et al.* (2017) synthesized the BCZT nanowires using simple, scalable sol-gel assisted template-wetting methodology and improved the temperature dependence of ferroelectric BCZT by controlling morphology and strain at nanoscale (Datta *et al.*, 2017). The sol-gel hydrothermal synthesis is an effective technique to control and optimize the particle size and shape induced superior electrical properties in ferroelectrics (Ghasemian *et al.*, 2017; Hanani *et al.*, 2020b; Hanani *et al.*, 2020a; Ji *et al.*, 2020). Recently, Aggarwal *et al.* (2022) has reported the effect of polar solvent (e.g., ethanol) on the structural phase transformation in perovskite-nanocrystals (e.g., CsPbBr₃ NCs) which opened up new possibilities for modulation in properties by exploiting structure-property relationship in perovskite materials (Aggarwal *et al.*, 2022).

Surface Modifications

The surface-modifications at nanoparticles using appropriate modifier (e.g., hydrogen peroxide (H₂O₂), polyvinylpyrrolidone (PVP), dopamine, polyimide (PI), naphthyl phosphate (NPh) *etc.*) to improve the ceramic-polymer interfacial faces in composites by their uniform dispersion even at high loading would be studied for enhanced energy density capabilities (Chary *et al.*, 2020; Fu *et al.*, 2015; Luo *et al.*, 2014; Patra *et al.*, 2018; Sadhu *et al.*, 2017; Wang *et al.*, 2020). Wang *et al.* (2020) has schematically shown the mechanism for improved interfacial interactions and bonding due to surface-modifications using different modifiers leading to enhanced energy density properties in BT/PVDF based polymer-nanocomposites. Fig. 24.

Zhou *et al.* (2011) showed the improved dielectric properties in PVDF-nanocomposites filled with surface hydroxylated BaTiO₃ (h-BT) nanoparticles. The strong interaction between h-BT filler and PVDF matrix due to bonding between hydroxide-group on h-BT surface and fluorine atom in PVDF led to improved dielectric properties. Fig. 25.

Polyvinylpyrrolidone (PVP) is a water-soluble amorphous polymer which has good adhesive properties with both polymers and ceramic nanoparticles. Fu *et al.* (2015) demonstrated a PVP-employed surface-modification technique to enhance the dielectric properties (Fu *et al.*, 2015). PVP act as surfactant to improve the ceramic-polymer interfacial interactions by homogeneous distribution of nanoparticles by preventing agglomeration of nanoparticles through the repulsive force that arise from its hydrophobic carbon chains interacting each other in a solvent (Patra *et al.*, 2018; Voronova *et al.*, 2018).

The spectroscopic techniques e.g., Fourier transform infrared FTIR and nuclear magnetic resonance NMR are useful in systematic investigation of interfaces for surface-modification studies using various modifiers (Aggarwal *et al.*, 2022; Eischens and Pliskin, 1958) analyzed the molecules and bonding to the solid state surfaces using infrared spectorscopy (Harrick, 1960; Hofer, 2002). FTIR and NMR are the important tools to confirm the improvement in ceramic-polymer interfacial interactions due to the formation of new bonds by introducing an appropriate modifier between the ceramic and polymer phases. The stretching, bending and vibration modes of new bonds formed result a characteristic bands in the FTIR and NMR spectra which can be easily detected and analyzed to verify the modifications at the surface of nanoparticles which is not much effecting the actual ceramic and polymer phase formation in composites (Wang *et al.*, 2020; Zhou *et al.*, 2011).

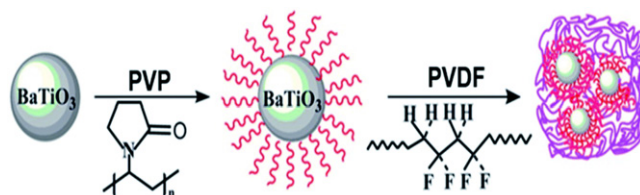


Fig. 25 Improvement in interfacial bonding with polyvinylpyrrolidone (PVP) modification on BT nanoparticles in BT/PVDF nanocomposites. Reprinted with permission from Ref. Fu, J., Hou, Y., Zheng, M., *et al.*, 2015. Improving dielectric properties of PVDF composites by employing surface modified strong polarized BaTiO₃ particles derived by molten salt method. *ACS Appl. Mater. Interfaces* 7, 24480–24491.

Orientation and Distribution of Nanofillers

Guo *et al.* (2022) proposed a sandwich-structural polymer-nanocomposite designing methodology to enhance the electrical properties by improving the regional distribution of electric field (Guo *et al.*, 2022). This work provides new thinking for the development of energy storage composite films by improving permittivity along with delay in electrical breakdown in composites. The multicomponent heterogeneous layered structure of ferroelectric PVDF, 2D boron nitride nanosheets BNNS, and linear dielectric polyimide PI also showed prominent energy storage properties in sandwich-structure films along with superior mechanical and thermal stability properties (Wu *et al.*, 2022).

The polymer-nanocomposites inspired nanograin engineering approach in normal ferroelectric Pb(Zr_{0.52}Ti_{0.48})O₃ (PZT) using aerosol deposition method to artificially induce relaxor behavior is also an effective designing methodology for high energy density capacitors (Jung *et al.*, 2020; Kim *et al.*, 2022). In aerosol-deposited PZT films, the high-speed impact of particles on substrate induced the formation of crystalline nanodomains within nanograins surrounded by highly disordered non-polar matrix enhanced the breakdown strength E_{BD} and slim P-E loop simultaneously to achieve ultrahigh storage energy density properties. It is the only known strategy for the formation of polar nanoregions (PNRs) to impart relaxor behavior in normal ferroelectrics with high E_{BD} in polycrystalline form (Ryu *et al.*, 2022).

Biodegradable and Renewable Solutions

The current efforts for sustainable energy resources include the development of renewable energy harvesting and storage devices. In this regard, developing the simple, efficient, environment friendly and sustainable ways to design and synthesize new functional materials are in demand. The recent work on biodegradable, renewable and flexible cellulose and boron nitride nanocomposites reported the energy storage density of 4.1 J cm⁻³ and breakdown voltage of 370 MV m⁻¹ with excellent thermal stability properties (Lao *et al.*, 2018).

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Complex Oxides: An Introduction

Paolo Ghigna, Department of Chemistry, University of Pavia, Pavia, Italy

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Metal oxides showing chemical complexity (*i.e.*, containing at least two different metals, or a metal in more than one oxidation state) are extremely important for applications in electronics.

It may seem strange that only three elements are enough to bring out the concept of "complexity". However, this is justified by the fact that, if we define a complex oxide as above, then the probability that one of the metals is a transition metal is rather large. Transition metal oxides (TMOs) are a central (if not *the* central) class of materials in Material Science. This is due to the fact that strong electronic correlations in these compounds give a complex interplay between structural, spin, orbital and charge degrees of freedom, thus leading to an extreme richness in their phase diagrams. Complex oxides, just to quote few examples, are known as magnetic, piezoelectric, ferroelectric, dielectric and superconducting materials. Diluted magnetic oxides play a crucial role in spintronic applications, and the development of Li-ion batteries was strongly indebted to the introduction of complex oxides as cathode materials.

In this brief introduction, I will review some of the aspects that, in my opinion, make complex oxides so worth of investigation for applications in electronics. This review is necessarily incomplete and biased, and the reader is referred to the excellent chapter of this section for more extensive information.

Many complex oxides of technological relevance adopt the perovskite crystal structure: perovskites display indeed a magnificent variety of crystal structures, making perovskites one of the favorite playgrounds for material scientists.

The archetypal perovskite structure is quite simple. Perovskites have general formula ABO_3 , and the prototypical structure is described by the $Pm\bar{3}m$ space group, with A in $1b$ sites ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), B in $1a$ sites (0, 0, 0) and oxygen in $3d$ sites ($\frac{1}{2}, 0, 0$). This structure can be seen as a regular 3D array of corner-sharing BO_6 octahedra, while the large A cation occupies the center of the cavities between octahedra. Such a structure is centrosymmetric and non-polar, but many materials with the perovskite structure undergo structural phase transitions. The low-symmetry structure often displays physical properties that are very different from the prototypical one, making these materials attractive for technological applications.

The ion displacement during the phase transitions can be classified as follows:

- 1) Displacement along a crystallographic direction. If cations move in a parallel direction, the resulting structure is polar and ferroelectric and piezoelectric materials are obtained.
- 2) Tilting of the octahedra around one or more crystallographic directions. As octahedra are all connected, the tilting of one octahedron leads to collective tilting. The resulting structures are many and have been classified in different ways.
- 3) Octahedra distortions, *e.g.*, as a result of Jahn-Teller cooperative distortions.
- 4) Combinations of displacement, tilting and distortions are possible.

The prototypical perovskite displaying a distortion of the first type is $BaTiO_3$, which, above $T_c \cong 135^\circ\text{C}$ is a cubic perovskite with the $Pm\bar{3}m$ primitive structure. On cooling, a structural phase distortion takes place, with the cations displacing along one of the cubic axis, with respect to the oxygen framework. The resulting structure is tetragonal (space group $P4mmm$) and polar, and the phase transition is associated with large anomalies in the dielectric properties. For this reason, $BaTiO_3$ and related materials are used as high dielectric materials for capacitors in the field of electronics. Lead titanate, $PbTiO_3$, which is the end member of the lead zirconate titanate family, $PbZr_xTi_{1-x}O_3$, one of the most widespread piezoelectric material, has the same tetragonal crystal structure.

The best-known example of a perovskite with tilted octahedra is strontium titanate, $SrTiO_3$. At room temperature, the crystal structure is cubic, but below $T_c \cong 105\text{K}$ a phase transition takes place to a structure where the octahedra tilt around the cubic c axis in an alternate way: the resulting crystal structure is tetragonal, with a doubling of the lattice constants: $a_T = 2a_C$, $b_T = 2b_C$, $c_T = 2c_C$. Besides being an excellent substrate for the epitaxial growth of thin films of various materials, including cuprate superconductors, the interface between strontium titanate and lanthanum aluminate is extensively studied since it displays a number of properties not shown by each of the two materials, including electrical metallic conductivity, ferromagnetism, large negative in-plane magnetoresistance, giant persistent photoconductivity, and superconductivity.

The history of oxide superconductors deserves a brief discussion. It started in 1986 with the discovery, by Bednorz and Müller at the IBM research laboratory in Zurich, of superconductivity at 35K in strontium-doped $LaCuO_4$ (lanthanum barium copper oxide, or LBCO). This discovery was a real breakthrough, as it was a common believing that BCS theory should outlaw superconductivity at temperatures above 30K: just one year after the discovery, in 1987, Bednorz and Müller were awarded the Nobel Prize in Physics. A quest for higher transition temperatures immediately started, and in the same year, it was found that, by replacing lanthanum with yttrium, thus making yttrium barium copper oxide, YBCO, or $YBa_2Cu_3O_{7-x}$, transition temperatures higher than the normal boiling point of nitrogen could be obtained. The transition temperature of YBCO is 92K. The discoveries of bismuth strontium copper oxide (BSCCO, in 1988), thallium barium calcium copper oxide (TBCCO, in 1988), and mercury barium calcium copper oxide (HgBCCO, in 1993) progressively shifted the highest transition from 92 to 108, 125 and 133K, respectively.

Structurally, all these complex oxides are related, and their structure is related to that of perovskite. Indeed, it was the interest of Bednorz in perovskites that led to the search of superconductivity in copper oxides. The structure of cuprate superconductors can be generally described as formed by conducting perovskite CuO_2 planes, spaced by insulating layers with the NaCl structure. The resulting

materials have then a layered structure, and the coupling between the CuO_2 planes is very small. This results in a strong anisotropy in electrical conductivity, which is much higher along the crystallographic a,b planes than along the c direction, which is perpendicular to the CuO_2 planes. The properties of these materials are then quasi 2D. The transition temperature depends on the chemical composition and the number of adjacent CuO_2 planes in the structure. For example, in the BSCCO family, Bi-2201, with one CuO_2 plane, has $T_c \approx 33\text{K}$, Bi-2212, with two adjacent CuO_2 planes, has $T_c \approx 96\text{K}$, and Bi-2223, with three adjacent CuO_2 planes, has $T_c \approx 108\text{K}$.

Copper is usually found in a mixture of Cu(II) and Cu(III) oxidation states. The ratio between Cu(III) and Cu(II) is crucial for determining T_c . The maximum of T_c is found in correspondence of the “optimal doping”, equivalent to a ratio $\text{Cu(III)}/\text{Cu(II)} \cong 0.16$.

Superconductivity in cuprates is still unexplained. The high transition temperatures and the fact that the isotope effect is small exclude the conventional BCS pairing mechanism mediated by electron-phonon coupling. The main problems in the understanding of superconductivity in oxides are related to the fact that they present strong correlation effects that, as explained above, are out of reach of conventional mean field theories. In addition, the investigation of pairing mechanisms different from electron-phonon interaction, such as involving plasmons, excitons, paramagnons, requires a significant expansion of current first-principles theory of the superconducting phase.

Nevertheless, cuprate superconductors have already found practical applications: the superconducting wires at the CERN large hadron collider, which are tens of kilometers in length, are made of Bi-2223, cooled down at 77K by liquid nitrogen.

Strong electronic correlations, which play a crucial role in the properties of oxide superconductors, are a widespread feature in complex oxides. Electronic correlations are the results of the competition between a kinetic energy term, deriving from the carrier mobility or hopping from site to site, and a potential energy term, deriving from the on-site Coulomb repulsion between charge carriers.

In terms of chemical bonding, electron are correlated if the overlap between orbitals is too small to give a significant bandwidth W . Defining U the on-site Coulomb repulsion, in the limit of $W/U < 1$, single particle band theory as described by LDA or Hartree-Fock approximations fails, and electrons cannot be considered as independent. On the contrary, each of the valence electrons in the material has a strong influence on each other. This situation is typical in oxides of 3d and 4f metals, where the incomplete valence shells of the metal give particularly narrow energy bands. The prototypical example is NiO, which is predicted by single particle band theory to be a metal, but it is an antiferromagnetic insulator. This behavior is due to the opening of a band gap in the Ni 3d states, due to the large on-site Coulomb repulsion, and resulting in the formation of two semibands (each of the semiband has half of the states of a “normal” energy band), called upper and lower Hubbard semibands. Particularly useful here is the Zaanen-Sawatzky-Allen classification, where the insulating state is named “Mott-Hubbard” or “charge transfer” if the filled oxygen 2p band lies in energy below or above the lower Hubbard semiband.

Mott insulating materials have been widely used for making transistors, where the phase transition between the insulating and metal state is used as a switch (Motttronics). For example, in LaTiO_3 the band filling can be tuned by modulating the oxygen stoichiometry, thus giving a fine tuning of its electronic properties. Other applications range from superconducting magnets to thermochromic materials for intelligent windows.

The mere fact that electron correlation defies single particle band theory makes the theoretical description of the electronic structure of these materials still quite difficult. Here, advanced experimental tools for the investigation of the magnetic and electronic structure are of fundamental importance, and among them, resonant X-ray scattering (RIXS) and neutron spectroscopies are receiving increasing consideration. Here, spectral feature emerges that are not explained by single particle theory, and are therefore attributed to correlation effects, and may be usefully compared with those predicted by given models.

An introduction to complex oxides would be incomplete without at least mentioning the spinel structure. The structure of spinel oxides, having formula AB_2O_4 , is described by space group $Fd\bar{3}m$, with the A in the 8a sites (0, 0, 0), B in the 16d sites (5/8, 5/8, 5/8), and oxide ions in the 32e sites (x, x, x , with $x \cong 0.375$). From the symmetry, it can be seen that the A cations are surrounded by 4 oxide ions in a tetrahedral geometry, while the B cations are surrounded by 6 oxide ions forming a distorted octahedron. Many ferrites, which are so relevant for applications as magnetic materials, display this crystal structure.

Oxide Surfaces

Giada Franceschi and Ulrike Diebold, Institute of Applied Physics, TU Wien, Vienna, Austria

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Abstract

The atomic details of metal oxide surfaces carry rich and tunable physics that can be exploited for various electronic applications. These details can be unveiled and rationalized through the surface science approach, which relies on single crystalline samples investigated under highly controlled conditions. Tremendous progress has been achieved in understanding and manipulating binary oxide surfaces at the atomic scale, closely followed by current research on multielement oxides. An overview is given through the examples of rutile $\text{TiO}_2(110)$, $\text{SrTiO}_3(110)$, and Sr-doped $\text{LaMnO}_3(110)$, which also highlights the important role of atomic defects and surface reconstructions in determining a material's macroscopic properties.

Nomenclature

AFM atomic force microscopy.
DFT density functional theory.
LEED low-energy electron diffraction.
LEIS low-energy ion scattering.
LSMO lanthanum-doped strontium manganite, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$.
PLD pulsed laser deposition.
STM scanning tunneling microscopy.
 V_O oxygen vacancy.
XPS X-ray photoemission spectroscopy.
UHV ultra-high vacuum.

Key Points

- The atomic-scale details of oxide surfaces can strongly affect a material's performance in many electronic applications. This motivates surface science studies on model oxide surfaces, characterized by reproducible, known structures.
- Local probes such as scanning tunneling microscopy afford to directly visualize (and/or manipulate) oxide surfaces at the atomic scale. Theoretical methods such as density functional theory can rationalize the experimental observations, build structural models, and gain mechanistic insights into fundamental surface processes and reactions.
- Comprehensive studies (experimental and theoretical) have been performed on binary oxides such as rutile $\text{TiO}_2(110)$. These lay the foundation for more complex, multielement materials at the core of emerging applications.
- Experiments have unveiled that multielement oxide surfaces are characterized by a rich variety of complex reconstructions with markedly different properties, which can be tuned by altering the surface's cation and anion composition. The rapid development of machine learning algorithms will enable to address the complexity of multielement oxide surfaces on the theoretical side.

Introduction

The increasing popularity of oxide materials for electronic applications (Coll *et al.*, 2019; Ray, 2021) calls for a deep understanding of their fundamental properties, particularly of their surfaces. After all, this is where the oxide interacts with the environment and/or other components in a device. Of growing interest are the atomic details of oxide surfaces: As shown in this review, these tend to deviate significantly from the ideal bulk phase. Point defects such as oxygen vacancies are common (Ganduglia-Pirovano *et al.*, 2007; Jupille and Thornton, 2015; Pacchioni, 2003) and so are surface reconstructions (Andersen *et al.*, 2018; Bliem *et al.*, 2014; Diebold, 2003; Franceschi *et al.*, 2021), i.e., cooperative modifications of the surface atomic and electronic structure that minimize the surface free energy and, in case of polar systems, prevent the polar catastrophe (Noguera, 2000).

The changes brought by point defects and surface reconstructions occur at the atomic scale and within a couple of layers only. Yet, they have a measurable, macroscopic impact on the oxide material: the new compositions, bonding environments, and electronic configurations that they entail can affect transport properties (Glass *et al.*, 2019; Tufte and Chapman, 1967) and reactivity (Pacchioni and Ferrari, 1999; Parkinson, 2019; Riva *et al.*, 2018; Schaub *et al.*, 2001), and even let physics unseen in the bulk phase emerge (Dudy *et al.*, 2016; Wang *et al.*, 2014a). Excitingly for fundamental and applied research, the surface atomic

details and related macroscopic properties can be tuned through several external stimuli. For instance, thermal treatments at differently oxidizing conditions (Batzill *et al.*, 2004; Berdunov *et al.*, 2004; Diebold, 2003; Dudy *et al.*, 2016; Franceschi *et al.*, n.d., Kraushofer *et al.*, 2018; Li *et al.*, 2009; Luches and D'Addato, 2016; Wagner *et al.*, 2014), strain (Berdunov *et al.*, 2004; Wang *et al.*, 2013), photon and electron irradiation (Glass *et al.*, 2019; Gurwitz *et al.*, 2014; Tan *et al.*, 2014; Zhao *et al.*, 2020), dilute doping (Franceschi *et al.*, 2020a, Hulva *et al.*, 2021; Meevasana *et al.*, 2011), exposure to gases (Rohr *et al.*, 1994; Schulz and Cox, 1992), and by interfacing different materials in epitaxial thin-film heterostructures (Chikina *et al.*, 2018; Christensen *et al.*, 2019; Huang *et al.*, 2018b; Miletto Granozio *et al.*, 2013). Modeling the atomic details of oxide surfaces and how they are affected by such external stimuli is the first step towards understanding and optimizing the materials' performance.

In the last decades, the exploration of the atomic details of oxide surfaces has been increasingly pursued through the so-called surface science approach, i.e., studies on idealized model systems (single crystals with well-defined orientation and surface atomic properties) under tightly controlled atmospheres (ultra-high vacuum, UHV, i.e., at pressures below 10^{-9} mbar) (Woodruff, 2016). These stringent conditions are essential to disentangle all the many factors that may participate in the atomic-scale physics of the investigated oxide surface. Many surface science techniques are available and each offers unique insights: scanning probe techniques (scanning tunneling microscopy, STM, and atomic force microscopy, AFM) yield real-space imaging of the surface with atomic resolution, and allow manipulation of atomic features; area-averaging spectroscopies (x-ray and ultra-violet photoemission spectroscopies, XPS and UPS; low-energy ion spectroscopy, LEIS; x-ray absorption spectroscopy, XAS; infrared absorption spectroscopy, IRAS) probe chemical compositions, cation oxidation states, and bonding environments; electron diffraction techniques (low-energy electron diffraction, LEED(-IV); reflection high-energy electron diffraction, RHEED; low-energy electron microscopy, LEEM; surface X-ray diffraction, SXRD) give quantitative structural information. Crucially, the controlled experimental conditions inherent to the surface science approach offer an ideal platform for computational modeling (often density functional theory, DFT), which can yield reliable models of the structures investigated. The importance of building such structural models cannot be overstated. Only when the atomic structure and intrinsic defects are well understood and controlled can the atomistic processes that drive the materials' performance be studied and rationalized.

Until recently, most efforts in the field of oxide surface science have been pivoting around binary oxide materials. Structural models have been established for differently oriented single crystals and (ultra-)thin films, including TiO_2 (Diebold, 2003; Dohnálek *et al.*, 2010; Pang *et al.*, 2008), In_2O_3 (Egdell, 2015; Wagner *et al.*, 2014), iron oxides (Parkinson, 2016), CeO_x (Mullins, 2015), ZnO (Wöll, 2007), SnO_2 (Batzill, 2006), MgO (Benedetti *et al.*, 2008), NiO_x (Kuhlenbeck *et al.*, 2013), CuO_x (Gattinoni and Michaelides, 2015), VO_x (Surnev *et al.*, 2003), MnO_x (Li *et al.*, 2009; Moller *et al.*, 2018), and WO_x (Doudin *et al.*, 2016). Tremendous progress has been achieved in understanding and modeling their surface properties, and how these affect fundamental processes occurring at surfaces. Similar investigations have been performed also on systems with more than one cation, such as ternary – e.g., SrTiO_3 (Andersen *et al.*, 2018; Sokolović *et al.*, 2019; Jupille, 2020), BaTiO_3 (Förster *et al.*, 2013; Morales *et al.*, 2014), LaAlO_3 (Kienzle *et al.*, 2015) – and multicomponent oxides, most notably doped, mixed-valence manganites (Franceschi *et al.*, 2020b; Franceschi *et al.*, 2021; Fuchigami *et al.*, 2009; Gambardella *et al.*, 2014; Kelley *et al.*, 2021; Ma *et al.*, 2005; Renner *et al.*, 2002; Rößler *et al.*, 2010; Tselev *et al.*, 2015). Much attention has also been given to the characterization of atomic defects and their manipulation, again mostly on binary oxides (Jupille and Thornton, 2015; Setvín *et al.*, 2017). Prominently featured in the recent literature are polarons, i.e., localized quasiparticles born from the coupling of excess charges with ionic vibrations that preferentially form in transition metal oxides, thereby affecting a variety of properties (Franchini *et al.*, 2021).

This review article focuses on three bulk oxide systems – rutile $\text{TiO}_2(110)$, $\text{SrTiO}_3(110)$, and Sr-doped $\text{LaMnO}_3(110)$ – aiming to give an overview of the striking complexity intrinsic to the atomic details of oxide surfaces, and how this richness may open up new avenues in electronic applications. Because the goal is to discuss the local properties of their surfaces, emphasis is laid on investigations performed through scanning probe techniques (mostly STM, as this is the most common local method to explore oxide surfaces (Setvín *et al.*, 2017)) and DFT calculations. STM affords the unique ability to directly “see” point defects and the details of surface reconstructions, and theory is essential to interpret the experimental observations. To keep this article concise, ultra-thin oxide films (one or two atomic layers, typically supported on metal substrates) are not discussed. Note, however, that these systems are the focus of an active field of research in their own right (Netzer and Fortunelli, 2016) and are of high technological interest: Due to their reduced dimensionality and the strong interaction with the substrate, the properties of ultrathin oxide films are highly tunable and typically different than those found on bulk crystals.

The first system to be discussed is rutile $\text{TiO}_2(110)$ (Section “Rutile $\text{TiO}_2(110)$ ”). Rutile $\text{TiO}_2(110)$ is the most investigated system in oxide surface science, and may be defined “simple”: in its stoichiometric or slightly reduced¹ form, it displays a bulk-truncated surface with isolated oxygen vacancies. Despite its simplicity, the case of rutile $\text{TiO}_2(110)$ goes to show that isolated point defects may produce interesting and technologically relevant effects (in this case bound to polarons, a hot topic in many disciplines besides surface science (Franchini *et al.*, 2021)), which can also determine the formation of new surface reconstructions (in the case of rutile $\text{TiO}_2(110)$, a (2×1) structure). Next, materials with more than one cation are tackled (see Sections “ SrTiO_3 : Atomic Properties and Reactivity” and “Sr-Doped $\text{LaMnO}_3(110)$ ”). For these, bulk-truncated terminations become the exception. Section “ SrTiO_3 : Atomic Properties and Reactivity” focuses on SrTiO_3 , the archetypal perovskite oxide. Its polar (110) termination is chosen to showcase one common way that oxide surfaces deal with polarity, i.e., by realizing surface reconstructions. The fact that SrTiO_3 has more than one cation introduces another degree of freedom, which causes the formation of not only two but of several surface reconstructions that are related by the Ti-to-Sr ratio in the near-surface region of the solid. After briefly describing

¹The term “reduced” is used in the chemical sense, i.e., deficient of oxygen or rich in excess metal cations in some form.

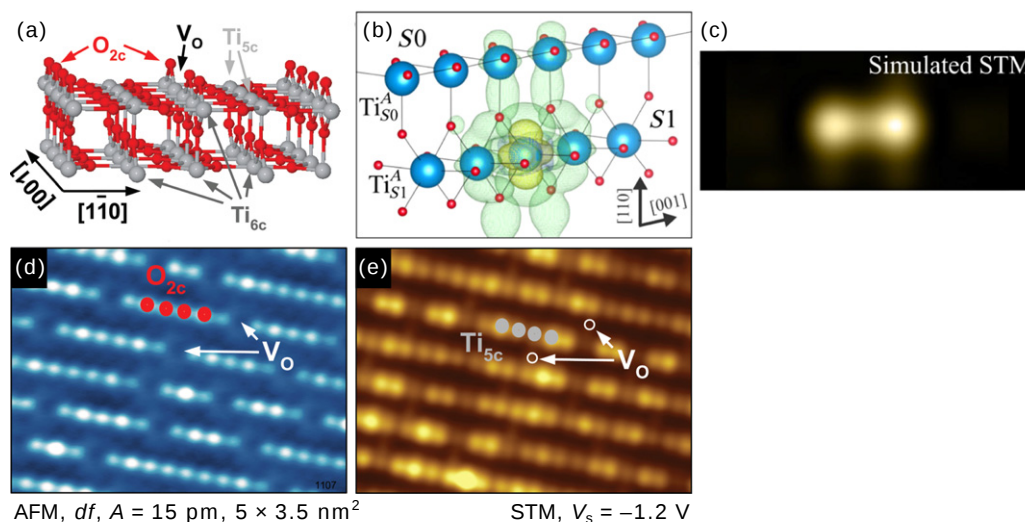


Fig. 1 The rutile $\text{TiO}_2(110)$ surface. (a) Structural model of rutile $\text{TiO}_2(110)$ with an oxygen vacancy (V_o) in the rows of 2-fold coordinated O atoms (O_{2c} , red). The other relevant surface atoms are 5-fold coordinated Ti_{5c} (gray). (b) Charge density isosurface of an isolated polaron sitting at a subsurface Ti^{3+} site (layer S1). The density cloud extends to the top Ti atoms (layer S0). (c) Corresponding filled-states STM image, simulated for a distance of at 2 Å from the surface. (d – e) Scanning probe imaging of the same area of a slightly reduced rutile $\text{TiO}_2(110)$ sample; i.e., a surface with coverage of a few percent V_oS . (d) Frequency shift in non-contact AFM. (e) Tunneling current in filled-states STM. Both images were measured at a sample temperature $T = 78 \text{ K}$ and in constant-height mode. They were acquired with a combined STM/AFM instrument operating with a q-plus sensor (Giessibl, 2009), which can detect the interaction forces between tip and sample (AFM) while registering the tunneling current (STM). Adapted from Reticioli, M., Setvín, M., Hao, X., *et al.*, 2017. Polaron-driven surface reconstructions. *Physical Review X* 7 (3), 031053. Setvín, M., Wagner, M., Schmid, M., Parkinson, G.S., Diebold, U., 2017. Surface point defects on bulk oxides: Atomically-resolved scanning probe microscopy. *Chemical Society Reviews* 46 (7), 1772. With permission from American Physical Society and Royal Society of Chemistry.

the $\text{SrTiO}_3(110)$ reconstructions, the Section discusses how the differences in their atomic-scale details affect the incorporation of oxygen in the material, an important process for energy conversion technologies based on perovskite oxides. Finally, Section “Sr-Doped $\text{LaMnO}_3(110)$ ” considers doped mixed-valence manganites through the example of Sr-doped $\text{LaMnO}_3(110)$, or LSMO (110). The variability in the oxidation state of Mn adds yet another degree of freedom at the surface, affecting the oxygen stoichiometry of the surface together with the cation stoichiometry. As a result, an even larger number of different reconstructions is observed as a function of the cation composition and oxygen chemical potential used to treat the surface, each characterized by unique properties.

Case Studies

Rutile $\text{TiO}_2(110)$

TiO_2 has long attracted interdisciplinary scientific interest, owing to its use as a support of both metal and oxide catalysts, a photocatalyst, an electron transport material in solar cells, a gas sensor, corrosion-protective coating, in electric devices such as memristors, and more (Diebold, 2003). In the surface science community, rutile $\text{TiO}_2(110)$ has been extensively used as the model system to unveil the fundamental processes driving these TiO_2 -based applications (Diebold, 2003; Dohnálek *et al.*, 2010; Pang *et al.*, 2008). The rutile $\text{TiO}_2(110)$ is the thermodynamically lowest energy surface of TiO_2 , i.e., the orientation that will spontaneously be exposed at equilibrium. Moreover, rutile $\text{TiO}_2(110)$ single crystals are inexpensive, readily available, and comparatively easy to prepare in UHV through cycles of ion sputtering and annealing. This system offers a nice example of the deep insights that can be gathered through a combination of scanning probe techniques and computational modeling.

The surface structure of rutile $\text{TiO}_2(110)$, in its stoichiometric or slightly reduced form (Fig. 1(a)), is unreconstructed, except for minor structural relaxations (Diebold, 2003; Pang *et al.*, 2008). It is composed of rows of topographically lower-lying 5-fold coordinated titanium ions (Ti_{5c}) and rows of topographically higher-lying two-fold coordinated oxygen ions (O_{2c})² running along the [001] direction. Following reduction, oxygen vacancies (V_oS) are formed within the O_{2c} rows. AFM gives a direct view of this surface (Fig. 1(d)). By terminating the AFM tip with an O atom, it is possible to achieve contrast on the oxygen lattice, such that the protruding

² O_{2c} are often called bridging or bridge-bonded O atoms (O_b or BBO in the surface science literature).

O_{2c} atoms are imaged in the repulsive regime and appear bright, while oxygen vacancies appear as missing spots in the O_{2c} rows (Reticcioli *et al.*, 2017).

The oxygen vacancies at the surface are responsible for the most interesting effects: They are the most reactive sites in (photo) catalysis (Dohnálek *et al.*, 2010) and cause the formation of polarons, which have an important role in many technologies (Franchini *et al.*, 2021). The study of polarons with surface science tools is relatively new (mainly in the last decade) and lively, and rutile $\text{TiO}_2(110)$ has been the model system of choice. Studies have shown that STM is an ideal tool to investigate these quasiparticles (Minato *et al.*, 2009; Papageorgiou *et al.*, 2010; Reticcioli *et al.*, 2017; Setvín *et al.*, 2014). First, because their formation is promoted at the surface, where the crystal lattice is more flexible and the necessary lattice relaxations cost less energy (Reticcioli *et al.*, 2018). Second, because of the strong dependence of the tunneling current on the surface's density of states. These trapped charges can be directly *seen* in filled-state images where only electrons in the bandgap can contribute to the tunneling current. Third, because of their local nature: Direct insights of polarons are not possible with traditional approaches, such as transport measurements (Kang *et al.*, 2018), optical spectroscopies (Yoon *et al.*, 1998), or electron paramagnetic resonance (Livraghi *et al.*, 2011). Finally, STM allows polaron manipulation through the interaction with tip-induced field and currents (Setvín *et al.*, 2015; Yim *et al.*, 2016), which can give fundamental insights into the functioning of redox-based switching memories. Early photoelectron diffraction experiments on rutile $\text{TiO}_2(110)$ (Krüger *et al.*, 2008) gave the first evidence that small polarons reside predominantly in subsurface Ti_{6c} sites. This was later confirmed by several theoretical works, starting with Kowalski *et al.* (2010), and is in full accordance with the work of Reticcioli *et al.* (2017) presented in Fig. 1(b), showing the charge density isosurface of an isolated polaron in the subsurface. The corresponding simulated filled-states STM image in Fig. 1(c) is consistent with experiments (Fig. 1(e)), while, as expected, polarons are not visible in AFM (Fig. 1(e)).

Polarons were also shown to have a role in the stabilization of given surface reconstructions (Reticcioli *et al.*, 2017), specifically the (2×1) reconstruction that forms on rutile $\text{TiO}_2(110)$ at sufficiently reducing conditions (Li *et al.*, 2000). When the system is treated at increasingly reducing conditions, the concentration of oxygen vacancies (and polarons) gradually increases, with a favored spacing of three lattice sites. At a threshold concentration, the repulsion energy between the polarons is too costly, and the surface transitions to a (2×1) structure with Ti_2O_3 stoichiometry.

The example of rutile $\text{TiO}_2(110)$ presented above shows that the physics of a trivial oxide termination – a bulk-truncated (1×1) – can become increasingly more complex when its stoichiometry is locally altered through the introduction of point defects. The next Section shows that the complexity explodes when another cation is added to the compound – e.g., Sr, to form SrTiO_3 .

2.2 SrTiO_3 : Atomic Properties and Reactivity

SrTiO_3 is the prototypical perovskite oxide, the cornerstone of oxide electronics, and the most investigated multielement oxide in the field of surface science. The appeal comes from the richness of its bulk, surface, and interface properties: Donor doping by chemical impurities (Spinelli *et al.*, 2010; Takahashi *et al.*, 2006), oxygen vacancies (Spinelli *et al.*, 2010), or field effects (Shibuya *et al.*, 2006; Takahashi *et al.*, 2006) can turn the same material into an insulator, a metal, or even a superconductor. Moreover, local enrichment of oxygen vacancies can induce confinement of electronic conductivity in the form of 2D electron gases (Dudy *et al.*, 2016; Wang *et al.*, 2014a, 2014b). These unique properties make this system and other related perovskite oxides protagonists in a varied array of integrated technologies (Bhalla *et al.*, 2000; Kumah *et al.*, 2020; Peña and Fierro, 2001; Zubko *et al.*, 2011). In all cases, the precise details of the surfaces and interfaces of the perovskite material play a key role: It is at the surface where reactions take place, and again it is at the surface that functionalities of interfacing materials in thin-film perovskite heterostructures are coupled.

The uses and promises of perovskite oxides in applications have stimulated many efforts for gaining a detailed (atomic-scale) understanding of SrTiO_3 low-index surfaces, particularly of the (001) termination, which is traditionally used as a substrate for perovskite oxide growth. The excellent overview in (Jupille, 2020) shows that the surface stoichiometry of $\text{SrTiO}_3(001)$ (and, as discussed below, also of other orientations and other multielement oxides) is highly sensitive to the preparation conditions. Several, markedly different surface reconstructions can be stabilized by varying the annealing temperature and duration, sputtering yield and duration, or by depositing small amounts of either Sr or Ti followed by high-temperature annealing. Each reconstruction is characterized by different oxygen and/or cation stoichiometry, and by unique symmetries and arrangements of the surface atoms. While several theoretical models have been proposed for the various structures, a full consensus has yet to be reached. This is partly because the preparation procedures (mostly annealing at differently reducing conditions for different durations) are not fully reproducible from UHV chamber to UHV chamber, making it hard to unambiguously determine the composition of the surface while correctly accounting for the effect of bulk reduction, defective sites, charge transfer, and cation segregation (Jupille, 2020).

Another question is whether a bulk-truncated (1×1) surface of $\text{SrTiO}_3(001)$ can be stabilized in UHV. While a (1×1) pattern has often been seen in LEED, the (1×1) unreconstructed lattice has been resolved at the atomic scale only after cleaving the surface in UHV by exploiting the crystals' incipient ferroelectricity (Sokolović *et al.*, 2019). Even then, point defects were present on the TiO_2 and SrO terminations in the form of $14 \pm 2\%$ Sr adatoms and Sr vacancies, respectively, and the structure was unstable upon annealing above 200°C (Sokolović *et al.*, 2021). The surfaces prepared by wet-chemical treatments that exhibit a (1×1) LEED pattern are typically annealed only below 600°C and show a C contamination in XPS (Nishimura *et al.*, 1999; Sokolović *et al.*, 2021). (Castell, 2002) and (Sokolović *et al.*, 2021) argued that the LEED pattern stems from the contribution of the crystalline bulk that lies underneath a disordered contamination layer.

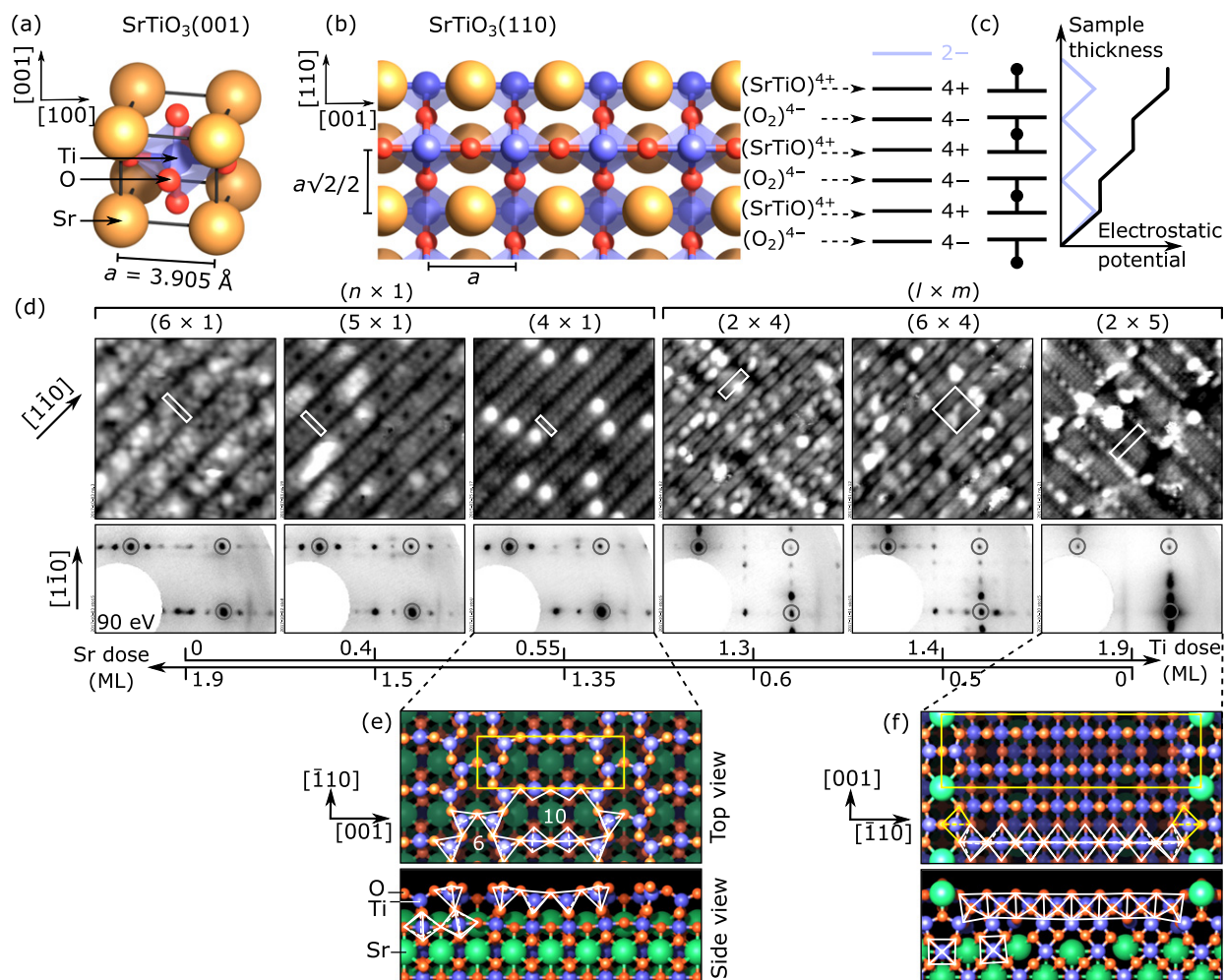


Fig. 2 Surface reconstructions compensating for the polarity of $\text{SrTiO}_3(110)$. (a) SrTiO_3 unit cell. (b) Bulk-truncated model of the (110) surface. Planes of opposite charge alternate along the $[110]$ direction, leading to a diverging electrostatic potential with increasing thickness as shown in panel (c). The polarity is compensated by introducing reconstructed surface layers with a formal charge of $-2e$. (d) Surface phase diagram of $\text{SrTiO}_3(110)$, as seen in empty-states STM (top row; $12 \times 12 \text{ nm}^2$ each; unit cells of each structure outlined in white) and LEED (bottom row; gray circles highlight bulk-derived diffracted beams). Deposition of small amounts of Ti or Sr (see bottom axis) followed by O_2 annealing allows moving along the phase diagram. One monolayer (ML) is the density of cation sites in a bulk-truncated $\text{SrTiO}_3(110)$ plane, i.e., $4.64 \times 10^{14} \text{ atoms/cm}^2$. (e, f) DFT models of the (4×1) and (2×5) reconstructions, respectively. Adapted from Riva, M., Franceschi, G., Lu, Q., *et al.*, 2019. Pushing the detection of cation nonstoichiometry to the limit. *Physical Review Materials* 3, 043802. Riva, M., Kubicek, M., Hao, X., *et al.*, 2018. Influence of surface atomic structure demonstrated on oxygen incorporation mechanism at a model perovskite oxide. *Nature Communications* 9 (1), 3710. With permission from Springer Nature.

Perhaps less controversial than the (001) surface of SrTiO_3 is the (110) termination, which also offers an example of surface polarity, a common and important phenomenon in oxide surface science (Goniakowski *et al.*, 2007; Noguera, 2000; Setvin *et al.*, 2018) and oxide electronics (Wang *et al.*, 2014a,b). According to the Tasker classification (Tasker, 1979), polar surfaces are defined as those whose repeat units bear a non-vanishing dipole moment. Because of this macroscopic dipole moment, these terminations are intrinsically unstable, and should never be observed. However, it is known that they can be stabilized by introducing compensating charges in the outer planes, achieved, e.g., by modifying the surface electronic structure and/or by changing the surface stoichiometry (Noguera, 2000). The (110) termination of SrTiO_3 exemplifies this: In its bulk-truncated form, it consists of alternating planes of $(\text{SrTiO})^{4+}$ and $(\text{O}_2)^{4-}$ (Fig. 2(b)), which produce a diverging electrostatic potential as a function of the thickness (Fig. 2(c)). Compensation of the diverging electrostatic energy is accomplished by realizing reconstructed TiO_x -rich layers (plus a few additional Sr atoms) on top of a bulk-truncated $(\text{SrTiO})^{4+}$ plane that bear a formal $-2e$ charge per bulk unit cell (Enterkin *et al.*, 2010; Wang *et al.*, 2014a; Wang *et al.*, 2013; Wang *et al.*, 2016).

Fig. 2(d) summarizes the thermodynamically stable surface reconstructions of $\text{SrTiO}_3(110)$ as they appear in STM and LEED. They are exceptionally stable due to their origin in the polarity compensation (Riva *et al.*, 2018). Each is

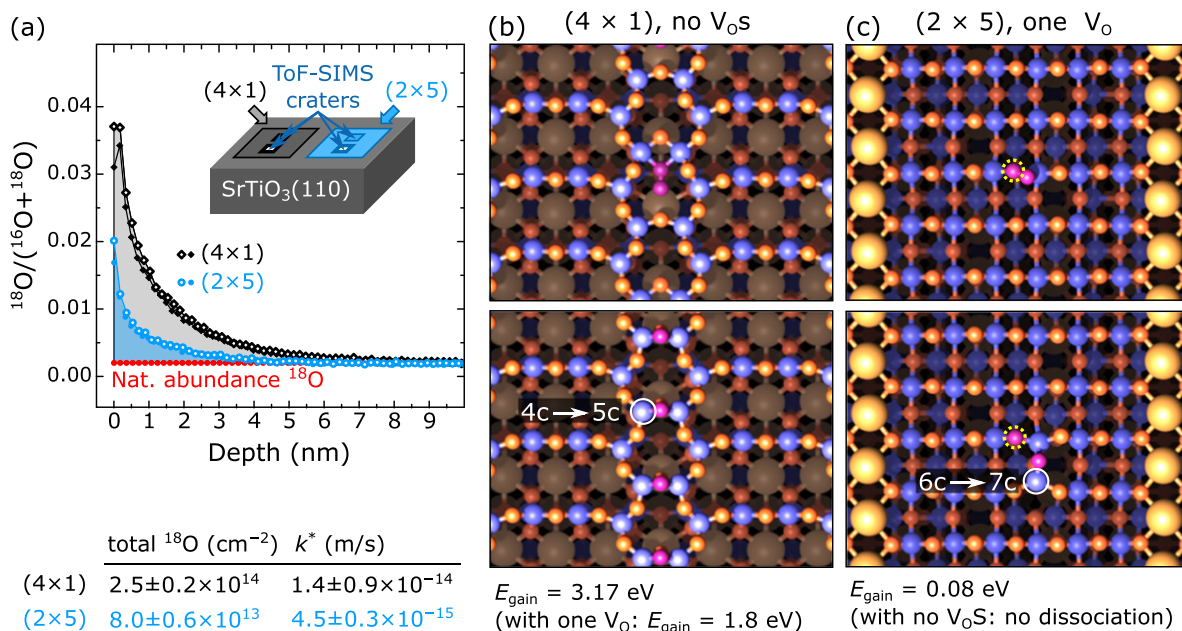


Fig. 3 Surface structure models and isotope exchange experiments on SrTiO₃(110). (a) ToF-SIMS $^{18}\text{O}_2$ isotope exchange depth profiles measured on two areas of a SrTiO₃(110) single crystal, prepared with surface layers with a (4×1) - (black) and a (2×5) - (blue) reconstruction, respectively. Full and open symbols correspond to two separate measurements on different spots on each half of this bi-crystal. (b, c) O₂ adsorption structures calculated by first-principles molecular dynamics DFT. Lowest-energy structural models for adsorption and dissociation of one O₂ molecule on the (4×1) surface without any surface vacancy (b), and on the (2×5) surface with one oxygen vacancy (c). Oxygen molecules do not dissociate on the $(2 \times n)$ without any oxygen vacancy. Adapted from Riva, M., Kubicek, M., Hao, X., *et al.*, 2018. Influence of surface atomic structure demonstrated on oxygen incorporation mechanism at a model perovskite oxide. Nature Communications 9 (1), 3710. With permission from Springer Nature.

characterized by a slightly different composition, which can be reversibly and reproducibly adjusted by depositing small amounts of Sr or Ti followed by high-temperature O₂ annealing (Riva *et al.*, 2019; Wang *et al.*, 2011) – see the bottom part of Fig. 2(d). Similar relations between surface reconstructions and composition are not unique to SrTiO₃(110). They were reported also for LaAlO₃(110) (Kienzle *et al.*, 2015), LiNbO₃(0001) (Levchenko and Rappe, 2008), BaTiO₃(001) (Kolpak *et al.*, 2008), PbTiO₃(001) (Saidi *et al.*, 2014), (001)- (Cook and Marks, 2018; Gerhold *et al.*, 2014), and (111)-oriented (Andersen *et al.*, 2018; Russell and Castell, 2008; Yang *et al.*, 2018) SrTiO₃, and for the (110)-oriented Sr-doped LaMnO₃ (Franceschi *et al.*, 2020b; Franceschi *et al.*, 2021) discussed below.

To appreciate the complexity of the surface reconstructions of complex oxides, and the extent to which reconstructions on the same material can differ from each other, it is instructive to take a closer look at those formed on SrTiO₃(110). They can be classified into two families – $(n \times 1)$ and $(l \times m)$ (see the left-, and right-hand sides of Fig. 2(d), respectively) – characterized by distinct properties. The $(n \times 1)$ series hosts networks of rings of corner-sharing TiO₄ tetrahedra residing on a bulk-like (SrTiO)⁴⁺ plane, as exemplified by the (4×1) structure shown in Fig. 2(e). Here rows of six-membered rings alternate with rows of ten-membered rings along the $[1\bar{1}0]$ direction. Adding to the complexity, the unit cell of the structure breaks the mirror symmetry of the bulk-truncated SrTiO₃(110) substrate underneath, causing the formation of two types of antiphase domain boundaries. On one type sit negatively charged TiO_x vacancy clusters, which relieve the strain between the SrTiO₃(110) bulk-truncated surface layer and the “ideal” reconstruction overlayer without boundaries (Wang *et al.*, 2013). To restore charge neutrality, positively charged Sr adatoms sit on the other type of domain boundary (Wang *et al.*, 2013), appearing as bright features in STM. On the other hand, the reconstructions belonging to the $(l \times m)$ series essentially consist of a double layer of octahedrally coordinated Ti, as exemplified by the (2×5) of Fig. 2(e): The subsurface layer hosts edge- and corner-sharing TiO₆ octahedra, while the top layer features sixteen edge-sharing TiO₆ octahedra, and two TiO₅ units that lack the apical oxygen atom, which alternate with five-fold coordinated Sr atoms with a two-fold periodicity along $[001]$ (Wang *et al.*, 2016). These Sr adatoms correspond to the bright dots visible in the STM image of Fig. 2(d).

The difference in the atomic details of the structures belonging to the $(n \times 1)$ and $(l \times m)$ series – the former consisting of a porous network of corner-sharing tetrahedrally coordinated TiO₄ units, the latter a bilayer of octahedrally coordinated TiO₆ units – makes for marked differences of their physical properties, as demonstrated by the work of Riva *et al.* (2018) (Fig. 3). The study used the two terminations as model systems for studying oxygen incorporation at perovskite oxide surfaces, a process that currently limits the efficiency of many energy conversion technologies based on perovskite oxides. Fig. 3(a) shows the time-of-flight secondary ion mass spectrometry (ToF-SIMS) data after isotopically labeled oxygen

($^{18}\text{O}_2$) exchange experiments without air exposure (4 h at 450°C and 0.1 mbar O_2). The (4×1) (black) has incorporated more oxygen than the (2×5) (blue), with a roughly three-time-larger exchange rate coefficient (k^*). The outcome is initially surprising if one considers the factors that are commonly considered most relevant for oxygen incorporation, such as (1) the availability and mobility of surface V_{OS} (the more V_{OS} , the easier the incorporation) (Bikondoa *et al.*, 2006; Kuklja *et al.*, 2013; Schaub *et al.*, 2001; Scheiber *et al.*, 2010); (2) the electronic effects that facilitate electron transfer (Chen *et al.*, 2013; Deskins *et al.*, 2010; Greiner *et al.*, 2012a,b); and (3) step density (steps are generally more reactive) (Gong *et al.*, 2006). Judging by these factors, the (2×5) should be more reactive than the (4×1) , since (1) it should accommodate surface oxygen vacancies more easily; (2) its smaller work function (as measured by XPS (Riva *et al.*, 2018)) should promote electron transfer to the incoming oxygen molecules; (3) it is characterized by a slightly higher step density than the (4×1) , as determined by STM. First-principle molecular dynamics simulations (Fig. 3(b) and (c)) revealed instead that the true determining factor behind the different reactivities of the two terminations toward O_2 dissociative adsorption and incorporation is their respective atomic details, specifically the degree of structural and chemical flexibility of their coordination polyhedra. When an oxygen molecule lands on the surface, the surface Ti atoms temporarily increase their coordination to host the to-be-incorporated oxygen. The (2×5) incorporates little oxygen because the surface TiO_6 units are rigid, and it is not favorable for them to further increase their coordination from six- to seven-fold (Fig. 3(c)). On the contrary, the TiO_4 polyhedra of the (4×1) are undercoordinated and flexible: They are more likely to distort and increase their coordination to five-fold and promote oxygen incorporation (Fig. 3(b)). This case exemplifies the strong role that the atomic details of oxide surfaces may have on the macroscopic properties of the material.

Sr-Doped $\text{LaMnO}_3(110)$

Moving from ternary to multielement oxides, the complexity increases further, and the number of available comprehensive atomic-scale studies decreases drastically. This is partly because of the lack of suitable samples and of the challenges in synthesizing high-quality single-crystalline films (Ojeda-G-P *et al.*, 2018), and partly because of the highly correlated electronic structure inherent in these materials, both in their bulk and at their surfaces (Mannhart and Schlom, 2010): Multielement oxides are extremely sensitive to minute alterations in their structure and stoichiometry. It is difficult to disentangle and interpret the different physical effects that may emerge under certain conditions. On the theoretical side, the description of highly correlated compounds is challenging and requires expensive, beyond-DFT methods.

So far, the scanning probe community has given most attention to high-temperature superconductive cuprates – mostly through scanning tunneling spectroscopy studies (Shen and Davis, 2008; Zeljko *et al.*, 2012) – and to doped manganites with the $\text{A}_{1-x}\text{B}_x\text{MnO}_3$ structure (Franceschi *et al.*, 2020b; Franceschi *et al.*, 2021; Fuchigami *et al.*, 2009; Gambardella *et al.*, 2014; Kelley *et al.*, 2021; Ma *et al.*, 2005; Renner *et al.*, 2002; Rößler *et al.*, 2010; Tselev *et al.*, 2015), where A is a rare-earth element and B is a divalent alkaline-earth element. Doped manganites are particularly appealing from a technological point of view: a rich phase diagram that includes doping- and thickness-dependent metal-to-insulator transitions, as well as (anti)ferromagnetic-to-paramagnetic transitions (Hemberger *et al.*, 2002; Junquera and Ghosez, 2003; Liao and Zhang, 2019), half-metallicity (Park *et al.*, 1998), and colossal magnetoresistance (Banik *et al.*, 2018) make them suited for various spintronics applications (Haghir-Gosnet *et al.*, 2004; Huang *et al.*, 2018a; Junquera and Ghosez, 2003; Majumdar and van Dijken, 2013) and integrated technologies based on thin-film heterostructures (Schlom, 2015; Zubko *et al.*, 2011). STM investigations on as-cleaved samples and in-situ grown films have revealed that this richness is reflected (if not enhanced) at the surface, via, e.g., the presence of small polarons (Ma *et al.*, 2005), the switching between insulating and metallic reconstructions as a function of the oxygen chemical potential (Fuchigami *et al.*, 2009), and the emergence of new properties at the interface between different materials in epitaxial heterostructures – among others, novel electronic (Nemes *et al.*, 2014), magnetic (Chen *et al.*, 2018; Hoffman *et al.*, 2016), and ferroic (Motti *et al.*, 2018) properties.

Lanthanum-strontium manganite ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$, or LSMO) is the prototypical doped manganite and perhaps the only multielement oxide whose surface structures have been systematically investigated in STM (Franceschi *et al.*, 2020b; Franceschi *et al.*, 2021). Fig. 4 summarizes the reconstructions that have been measured on (110) single crystalline $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ films grown on $\text{SrTiO}_3(110)$ substrates (Franceschi *et al.*, 2021). Some of them possess “simple” unit cells, like (1×1) or (2×1) , but most are characterized by significantly larger periodicities that cannot be expressed in the simplified Wood notation. Because of this, and because each structure entails different cation and oxygen composition (see Fig. 4(c)) and different valence of the Mn ions (as judged by XPS data, Franceschi *et al.*, 2020b), establishing structural models is challenging.

Like for the case of $\text{SrTiO}_3(110)$ discussed above, the (110) orientation of LSMO is polar, and the observed reconstructions are likely to form to compensate for the polar catastrophe. Another similarity is that the reconstructions are linked by near-surface stoichiometry: it is possible to switch them by depositing small amounts of manganese- or lanthanum-oxide plus O_2 annealing (Franceschi *et al.*, 2020b). Additionally, the surface structures can be tuned by treating the samples at different oxygen chemical potentials (Franceschi *et al.*, 2021) (μ_{O} , as determined by the substrate temperature and oxygen background pressure to which the surface is exposed). When annealing at 700°C and above 2×10^{-3} mbar O_2 , the structures on the left-hand side of Fig. 4(a) are stable and can cover the whole surface – if the surface stoichiometry allows it. When these structures are annealed at more reducing conditions, Mn moves across the surface, which phase-separates into patches of A-site-rich areas, and patches of Mn-richer reconstructions (Fig. 4(c)). The work in (Franceschi *et al.*, 2021) shows that by evaluating the relative coverages of the co-existing phases and knowing the average cation composition of the surface (which is preserved during the annealing treatments), it is possible to determine the composition of each phase through a simple lever rule and to establish a surface phase diagram as a function of the

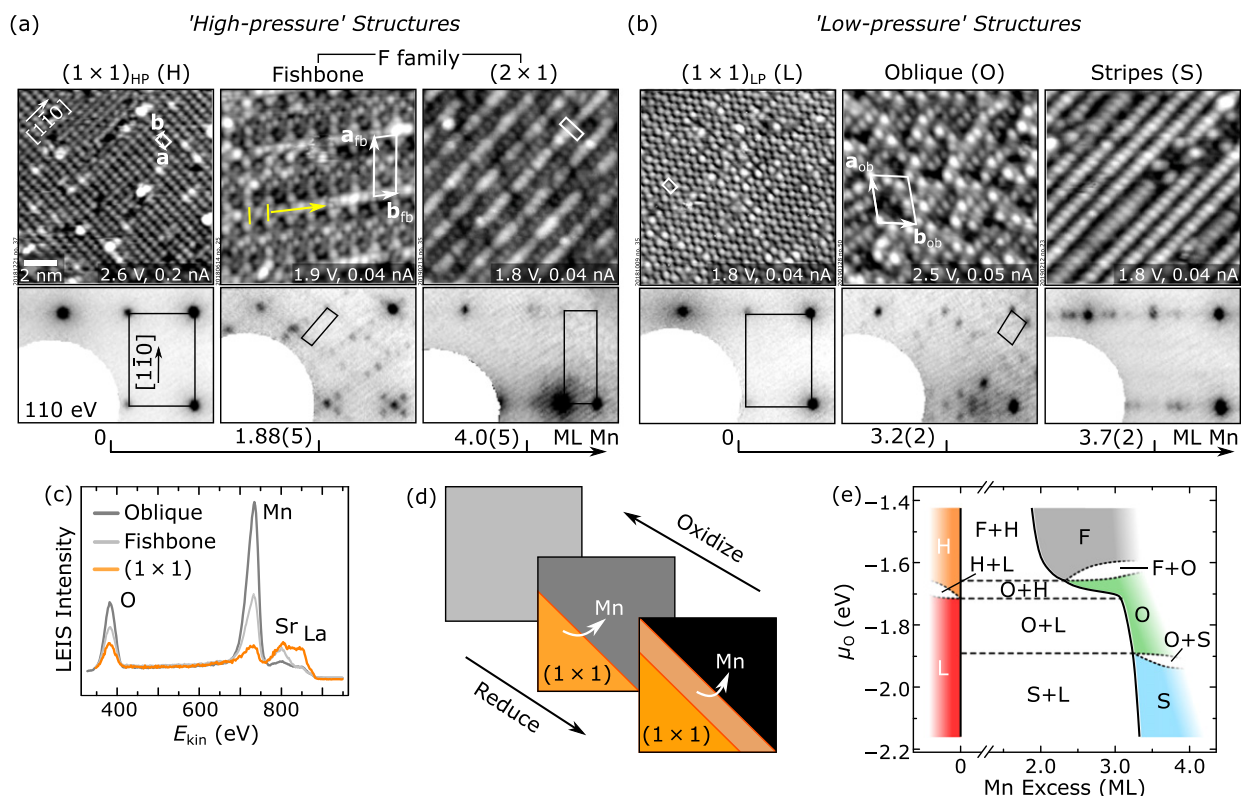


Fig. 4 Surface structures and phase diagram of epitaxial, (110)-oriented LSMO thin films. (a) “High-pressure” structures, obtained by tuning the surface composition by depositing controlled amounts of manganese- or lanthanum-oxide in PLD followed by O_2 ($p = 0.2$ mbar) annealing at 700°C . (b) “Low-pressure” structures, obtained by annealing the high-pressure phases below 2×10^{-3} mbar. (c) Comparison of LEIS spectra of some monophase structures. (d) Sketch of the (reversible) phase separation occurring during annealing: high-pressure structures tend to phase-separate in an A-site rich structure and Mn-richer structures by displacing Mn across the surface. (e) Surface phase diagram of LSMO(110) as a function of the oxygen chemical potential and the content of Mn at the surface. Adapted with permission from Franceschi, G., Schmid, M., Diebold, U., Riva, M., 2021. Two-dimensional surface phase diagram of a multicomponent perovskite oxide: $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3(110)$. *Physical Review Materials* 5.

oxygen chemical potential and the cation composition such as that of Fig. 4(d). Such a phase diagram is the first step for establishing reliable structural models, as it unambiguously determines the surface compositions and stability regions of the measured surface structures over a wide range of parameters.

Conclusions and Outlook

This review has presented three examples of bulk oxide surfaces of increasing complexity – rutile $\text{TiO}_2(110)$, $\text{SrTiO}_3(110)$, and Sr-doped $\text{LaMnO}_3(110)$ – to showcase the richness that lies within the atomic details of oxide surfaces. Scanning probe microscopies combined with theoretical insights have unveiled that their surfaces – and, as a result, the material’s macroscopic properties – are strongly affected by several intertwined factors, including stoichiometry, bulk polarity, density and nature of point defects, coordination and arrangement of the surface atoms, and cations’ oxidation state.

The example of rutile $\text{TiO}_2(110)$ demonstrates the comprehensive, atom-by-atom understanding that has been achieved for a few binary oxides, which has allowed to directly view, rationalize, and even manipulate their surface atomic details with exquisite precision (Setvín *et al.*, 2017). However, the road is still long for more complex, multielement compounds. As demonstrated here, these systems tend to exhibit a large variety of complex reconstructions. These strongly adapt to changes in stoichiometry, which concurrently affect the physical properties of the surface (Riva *et al.*, 2018). The variability and tunability are the very reasons that make multielement oxides appealing from application and fundamental standpoints, but are also what make their experimental control and computational modeling challenging. Nonetheless, progress is on the way: By establishing surface phase diagrams over a wide range of parameters, experimentalists are now able to unambiguously determine the compositions and stability regions of the various phases (Franceschi *et al.*, 2021); on the theoretical side, machine learning is rapidly becoming a new paradigm in materials simulations (Bartók *et al.*, 2017; Jinnouchi *et al.*, 2020; Zuo *et al.*, 2020), which will afford to explore a larger parameter space much more quickly, and deal with multivalent compounds in an economic and accurate manner.

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Electronic Properties of Complex Oxides

Ryan L Arevalo and Matthias Vandichel, Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick, Ireland

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Abstract

Complex oxides are of profound interest from scientific and technological point of view. Understanding their unique electronic properties requires a sophisticated treatment of the strong Coulomb interaction between electrons in well localized metal d- or f- orbitals and oxygen p states, which strongly hybridize with each other. This article will review the electronic properties of complex oxides and the state-of-the-art methods for investigating their electronic structures, whose applications transcend a wide area of scientific and technological disciplines, ranging from fuel cell electrodes and piezoelectric transducers to high temperature superconductors and spintronic devices.

Key Points

- The Zaanen-Sawatzky-Allen framework for identifying the electronic properties of transition metal oxides is discussed.
- Electronic structure calculation methods for strongly correlated oxides are presented.
- A review of previous studies investigating the electronic properties of specific complex oxides is presented.

Introduction

The unique electronic properties of complex oxides lay the foundation for the synthesis and design of materials for modern electronic devices with various commercial applications. These materials are used in electrodes and electrolytes in solid oxide fuel cells (Ishihara, 2009), piezoelectric transducers and actuators (Dahiya *et al.*, 2009), random access memory devices (Akinaga and Shima, 2010), high temperature superconductors (Shen and Dessau, 1995), and other technological applications in spintronics (Felser and Fecher, 2013). The notable electronic properties of these oxides often come from their strongly correlated electrons in d or f orbitals. In transition metal oxides such as NiO and MnO, unusual electronic properties stem from the strong Coulomb interaction between electrons in the well localized 3d-orbitals and the strong chemical bonding due to a large hybridization with oxygen 2p-orbitals (Poteryaev *et al.*, 2004; Lichtenstein, 2013). A delicate balance between such Coulomb interaction and chemical bonding yields a variety of interesting properties for these materials. In this article, a scheme to understand the electronic properties of complex oxides will first be discussed, followed by the electronic structure methods that are commonly used for this type of material, and finally, we will wrap up with some specific oxides whose electronic properties are important in various industrial applications.

Electronic Properties

In 1937, the established distinction between metals and insulators based on the analysis of their band structures was challenged when several simple transition-metal oxides with a partially filled d-electron band were found to be insulators (de Boer and Verwey, 1937). Mott (1949) attributed this observation to the strong on-site electron-electron interaction or the electron correlation U , which splits the original d-band into two bands with an energy gap that is characteristic of an insulator. Such strong Coulomb repulsion between electrons forces them to localize in atomic-like orbitals (Mott localization). Strongly localized electrons cannot move freely between atoms; rather, they jump from one atom to another neighboring atom by a “hopping” mechanism with an amplitude t that is proportional to the dispersion or bandwidth of the valence electronic states. The existence of the band gap can be understood as the competition between the Coulomb interaction or Coulomb correlation U , responsible for electron localization, and the transfer integral t of the tight binding approximation of the d electrons between neighboring atoms.

A simple model that considers this on-site repulsion between electrons is the Hubbard model, which can be used to explain the transition between the conducting and insulating behaviors of these materials. In this model, the Hamiltonian includes an additive Hubbard term $\mathcal{H}$, that explicitly defines the on-site electronic interactions:

$$\mathcal{H} = -t \sum_{ij,\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (1)$$

Here, $c_{i\sigma}$ and $c_{i\sigma}^\dagger$ are the fermionic annihilation and creation operators at site i , respectively, and $h.c.$ the Hermitian conjugate or $c_{i\sigma}^\dagger c_{j\sigma}$, while $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ is the number operator for electrons of spin σ on site i . Therefore, $c_{i\sigma}^\dagger c_{j\sigma}$ describes the destruction of an electron of spin σ on site j and its creation on site i , and vice versa for its Hermitian conjugate. The on-site Coulomb repulsion term U is proportional to the product of the occupation numbers of atomic states on the same site, while the hopping amplitude t is proportional to the bandwidth (or dispersion) of the valence electrons. In other words, the first term in Eq. (1) represents a kinetic

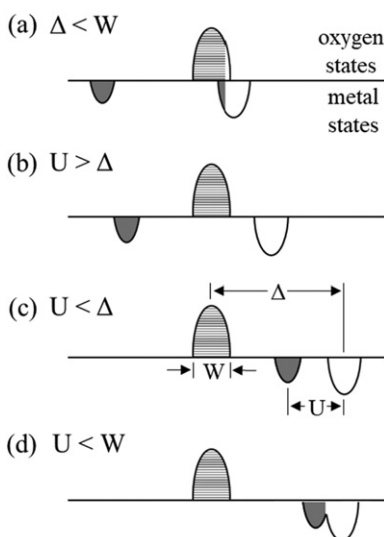


Fig. 1 A schematic diagram of the Zaanen-Sawatzky-Allen framework for metal-oxides showing three parameters in the density of states: Coulomb correlation U , charge transfer energy Δ , and bandwidth W . Four cases are shown: (a) semi-metal, (b) charge-transfer insulator, (c) Mott-Hubbard insulator, and (d) low U metal. The shaded and unshaded regions denote the occupied and unoccupied states, respectively.

energy, while the second term describes a potential energy or interaction energy. A band gap develops when electrons do not have sufficient energy to overcome the repulsive potential of other electrons on the neighboring sites (*i.e.*, $t < U$). Therefore, the balance between U and t controls the behavior of these systems and the character of their electronic ground state.

Considering this concept, a simple scheme in determining the metallic or insulating behaviors of transition metal oxides was proposed by Zaanen, Sawatzky and Allen (Zaanen *et al.*, 1985). In this model, a system of identifying the metallic or insulating oxides is based on three main parameters: the bandwidths W of occupied oxygen 2p states and metal d orbitals; the charge transfer energy Δ (*i.e.*, energy difference between oxygen 2p and the lowest unoccupied metal orbital); and the Coulomb correlation U , which is the energy difference between the highest occupied and lowest unoccupied metal orbitals. These parameters are shown in Fig. 1.

If the bandwidth W is larger than Δ or U , the oxide exhibits a metallic property, as shown in Figs. 1(a) and (d). This is true for oxides such as ScO and TiO, where the splitting between d-states due to Coulomb correlation is smaller than the bandwidth. For these two metallic cases shown in Fig. 1, the partially filled metal orbitals contribute to charge transfer. This can be seen in the overlap of the occupied 2p oxygen valence state and an unoccupied metal conduction state in Fig. 1(a), and the overlap of the occupied and unoccupied metal orbitals in Fig. 1(d). If the charge transfer energy Δ is larger than U , the oxide is a Mott-Hubbard insulator, where the band gap is of the d-d type as shown in Fig. 1(c). Here, the oxygen p level contributes only through virtual processes since it is much lower than the transition metal d level. On the other hand, when Δ is smaller than U , the oxide is a charge-transfer insulator. As shown in Fig. 1(b), the oxygen p band is located between the upper and lower metal d bands, and the band gap is of p-d type. In this case, the charge gap in the Mott-insulating state is by the charge transfer type, and the holes doped into the Mott insulator mainly occupy the oxygen p band.

Fig. 2 shows the Zaanen-Sawatzky-Allen plot, which categorizes the various transition metal oxides into Mott-Hubbard or charge transfer insulator, based on the relative magnitudes of the Coulomb interaction energy U and the p-d charge transfer energy Δ . The two regimes are separated by the $U = \Delta$ line. In reality, this $U = \Delta$ boundary is a crossover region where the charge gap character changes continuously without a sharp border. In general, late transition metal oxides (such as Cu oxides) are classified as typical charge-transfer insulators because of their characteristic large Coulomb repulsion energy U and small charge transfer energy Δ . On the other hand, early transition metal oxides (such as Ti and V oxides) are characterized by the small U and large Δ , and are thus classified as typical Mott-Hubbard insulators. As shown in Fig. 2, the experimental values of U and Δ from the analysis of 2p core-level photoemission spectra (Bocquet *et al.*, 1996) suggest that many early transition metal oxides are intermediate between the charge transfer and Mott-Hubbard regimes.

Electronic Structure Calculation Methods

One successful method of describing the electronic ground state structures of materials is the density functional theory (DFT), which is primarily based on the electron density $\rho(\mathbf{r})$, as opposed to the many-body electron wave function, $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$. The traditional wave function-based approaches and modern DFT methodologies to electronic structure calculations have several distinct similarities. First, the single-electron orbitals that comprise the many-body wave function are analogous to the Kohn-Sham orbitals in the DFT framework. Second, both approaches tend to be constructed via a self-consistent field (SCF) approach that requires matrix elements that are very similar. However, these methods have important differences in the treatment of electron correlation. In the many-body wave function approach, correlation effects are incorporated in post-SCF calculation methods that

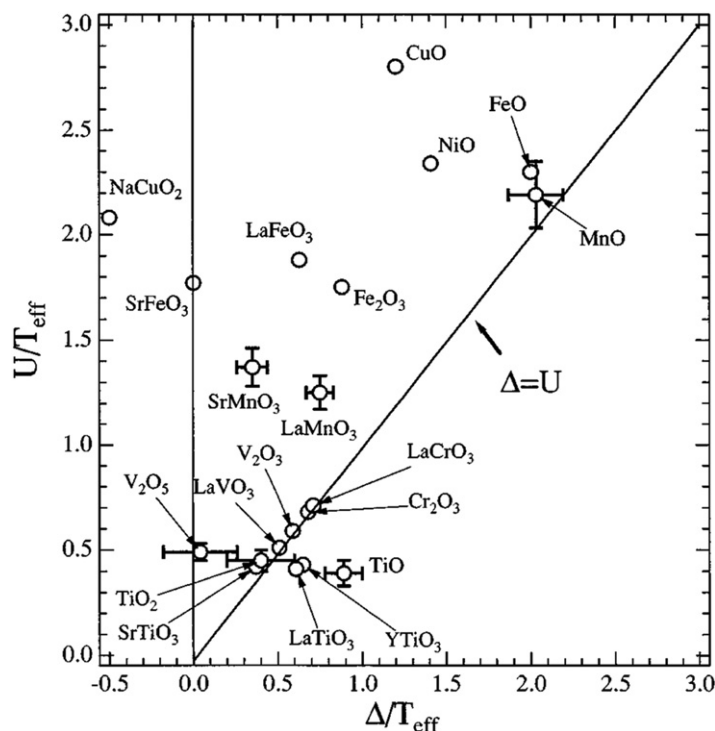


Fig. 2 The Zaanen-Sawatzky-Allen plot for 3d transition metal oxides across the Ti to Cu series. Δ and U (in eV) have been normalized by the effective hybridization strength T_{eff} . The $\Delta = U$ line separates the charge-transfer regime (above the line) and the Mott-Hubbard regime (below the line). Compounds falling close to the line are intermediate between these two regimes. Reprinted with permission from Bocquet, A., Mizokawa, T., Morikawa, K., *et al.*, 1996. Electronic structure of early 3d-transition-metal oxides by analysis of the 2p core-level photoemission spectra. *Physical Review B* 53, 1161. Copyright 1996 by the American Physical Society.

are computationally very expensive compared to the actual SCF procedure. On the other hand, DFT relies heavily on unknown exchange-correlation energy functionals, which are constantly being developed to achieve an arbitrary level of accuracy.

Different wave function-based electron correlation methods have been used primarily to introduce corrections to the standard Hartree-Fock (HF) method (Hartree, 1957; Fock, 1978) for many-body quantum systems. Such need arises from the underlying assumption of the HF approximation that electrons move independently within molecular orbitals under the influence of an averaged field induced by the other electrons. Such approximation completely fails when one considers molecular systems that are far from their ground-state equilibrium or in cases of weakly bound molecular complexes, where the description of electron correlation plays an important role. The electron correlation effects in the HF theory are usually included using standard *ab initio* correlation methods such as the configuration interaction, Møller-Plesset perturbation theory (Møller and Plesset, 1934), or coupled-cluster theory (Heßelmann, 2011; Coester, 1958; Coester and Kümmel, 1960), which are conventionally very expensive computationally. Fortunately, the development of new computational algorithms (such as density fitting and Cholesky decomposition) has led into an increased computational feasibility of these methods for extended molecular systems (Zienau *et al.*, 2009; Røeggen and Johansen, 2008; Koch *et al.*, 2003; Jung *et al.*, 2005; Polly *et al.*, 2004; Werner *et al.*, 2003). However, one has to be practically restricted to those methods that have the lowest scaling behavior with respect to the number of electrons N , such as the second-order Møller-Plesset perturbation theory (MP2) and the coupled-cluster with singles and doubles excitation (CCSD), which scale as $O(N^5)$ and $O(N^6)$, respectively (Heßelmann, 2011). A related method to the coupled cluster doubles theory is the random phase approximation (RPA), which includes part of the electron correlation energy explicitly to capture important physical effects without excessively increasing the computational cost (Chen *et al.*, 2017). RPA is the lowest level of theory that correctly describes electron screening and dispersions interactions without empirical corrections. Unlike the MP2 perturbation theory, RPA is insensitive to the size of the noninteracting gap and can even be applied to metallic systems (Chen *et al.*, 2017; Harl and Kresse, 2009).

Another serious problem with the HF method is the overestimation of the Coulomb interaction parameters (15–20 eV) and band gap values that are a factor of 2–3 larger than experimental values. This error stems from neglecting the screening effect on an interparticle interaction (Poluektov, 2004). In the HF method, it is assumed that there exists a uniform static background of positive charges that compensates the direct Coulomb interaction energy. However, the exchange energy is calculated in the same way as for gas particles with Coulomb interaction without regard to such positive background, which is well known to have a screening effect on an interparticle interaction (Poluektov, 2004). An improved method to address this problem is the so-called GW approximation, which may be regarded as an HF method with a frequency- and orbital-dependent screening of the Coulomb

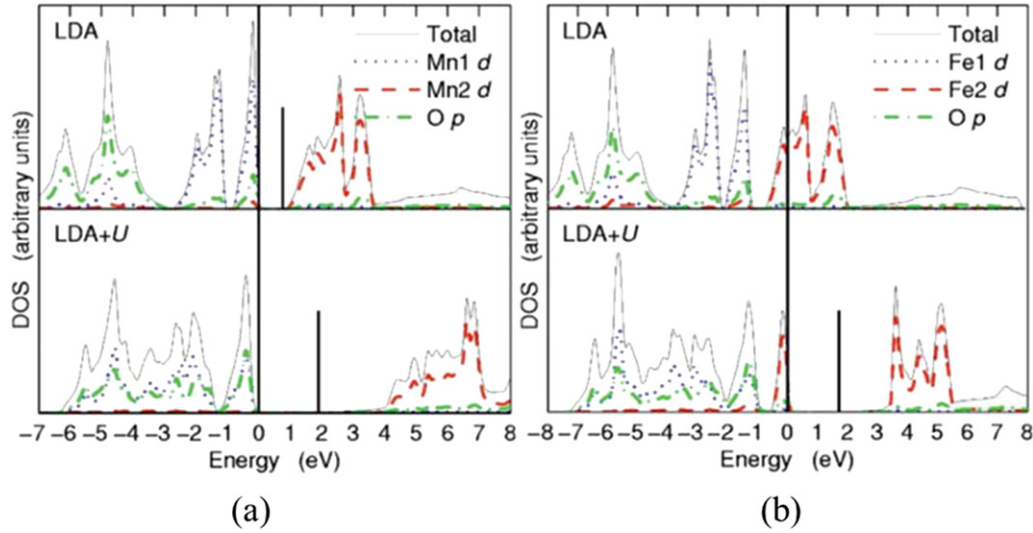


Fig. 3 A comparison of the DOS for (a) MnO and (b) FeO calculated using LDA and LDA + U. Reprinted with permission from Tran, F., Blaha, P., Schwarz, K., Novák, P., 2006. Hybrid exchange-correlation energy functionals for strongly correlated electrons: Applications to transition-metal monoxides. *Physical Review B* 74, 155108. Copyright 2006 by the American Physical Society.

interaction (Anisimov *et al.*, 1997; van Setten *et al.*, 2013). In this approximation, the self-energy is expanded in a formal Taylor series of the single particle Green's function G and the screened Coulomb interaction W . However, this method is computationally expensive and is not usually practical to use for large and complex systems.

Both the HF and DFT methods employ approximations to the total energy of the system. In DFT, electronic interaction energies are simply described as the sum of Coulombic repulsion between electronic densities in a mean field way (Hartree term) and an exchange-correlation functional, which is a function of the electronic charge density. Since the many-body features of an N -electron system cannot be adequately represented by an exchange function that depends on electronic charge density, correlated systems are poorly described by the standard DFT calculations. One problem in the implementation of DFT for correlated systems is the tendency of the exchange-correlation functional to over-delocalize valence electrons and over-stabilize metallic ground states (Himmetoglu *et al.*, 2014). This makes DFT inadequate in correctly predicting the properties of systems whose ground state is strongly characterized by a more pronounced localization of electrons such in the case of correlated systems.

One standard implementation of DFT for many materials is within the Local Density Approximation (LDA), wherein the exchange-correlation potential is approximated using a homogeneous electron gas model. However, the validity of LDA breaks down when applied to strongly correlated materials like complex oxides that contain transition metal or rare-earth metal ions with partially filled d- (or f-) shells. Instead of well localized d-electrons and sizeable band gap for transition metal oxides, LDA yields a partially filled d-band with metallic type electronic structure and itinerant d-electrons. For this reason, several approaches to improving the LDA for strongly correlated systems have been proposed. One of the popular approaches is the Self Interaction (SIC-LDA) method, which reproduces well the localized nature of the d-electrons in transition metal compounds (Svane and Gunnarsson, 1990). However, this method produces one-electron energies that are in strong disagreement with spectroscopic data, and that its predicted occupied d-bands for transition metal oxides are much below the oxygen valence band. Also, systems with weaker correlation effects may suffer from the overlocalization of the orbitals within the SIC framework.

One of the corrective approaches employed to relieve the mentioned band gap problem that arise from the use of the LDA is the LDA + U method, which has been a successful and computationally simple scheme for magnetic oxides and other strongly correlated materials (Anisimov *et al.*, 1991, 1997). The LDA + U method works similarly with the standard LDA orbital-independent one-electron potential to describe the valence electrons, while the strongly correlated electronic states (typically, localized d or f orbitals) for which the Coulomb d-d correction should be taken into account are treated using the Hubbard model. Within the LDA + U, the total energy of the system can be written as follows:

$$E_{LDA+U}[\rho(r)] = E_{LDA}[\rho(r)] + E_{Hub}[\{n_{mm'}^{I\sigma}\}] - E_{dc}[\{n^{I\sigma}\}] \quad (2)$$

Here, the E_{Hub} term contains the electron-electron interaction as modeled in the Hubbard Hamiltonian, while the E_{dc} term is the "double counting" correction that eliminates from E_{LDA} the part of the interaction energy that is already contained in the E_{Hub} . Using the LDA + U orbital-dependent potential reproduces qualitatively the correct description for Mott-Hubbard insulators, generating the upper and lower Hubbard bands with energy separation equal to the parameter U . Note that the Hubbard correction is only applied to the localized states of the system, and is a functional of the occupation numbers that are often defined as projections of the occupied Kohn-Sham orbitals (ψ_{kv}^σ) on the states of localized basis set (ϕ_m^I):

$$n_{mm'}^{I\sigma} = \sum_{k,v} f_{kv}^\sigma \langle \psi_{kv}^\sigma | \phi_m^I \rangle \langle \phi_m^I | \psi_{kv}^\sigma \rangle \quad (3)$$

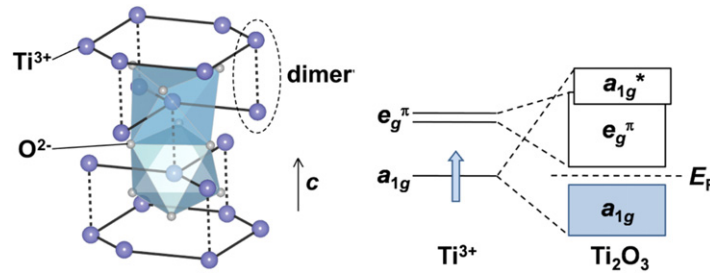


Fig. 4 Left: The rhombohedral unit cell of the Ti₂O₃ corundum structure. The Ti-Ti dimer along the z-direction is shown by the dashed line. Right: schematic representation of the t_{2g} splitting in Ti₂O₃. For clarity, the notation e_g^π indicates both $e_g^{\pi*}$ and e_g^π bands, as the $e_g^\pi - e_g^{\pi*}$ splitting is small. Reprinted with permission from Uchida, M., Fujioka, J., Onose, Y., Tokura, Y., 2008. Charge dynamics in thermally and doping induced insulator-metal transitions of (Ti_{1-x}V_x)₂O₃. *Physical Review Letters*, 101, 066406. Copyright 2008 by the American Physical Society

Here, f_{kv}^σ are the Fermi-Dirac occupations of the Kohn-Sham states, with k and v as the k-point and band indices, respectively. Using this occupation number in the LDA + U total energy functional results in the presence of the projection operator in the Hamiltonian. Thus, the most straightforward scheme is to use atomic-orbital type basis sets. The first formulations of the LDA + U were based on linear muffin-tin orbital (LMTO) implementation (Anisimov *et al.*, 1991). Thus, the natural choice to define on-site occupations are the localized muffin-tin-orbitals (MTO), constructed using Bessel, Neumann and Henkel spherical functions and spherical harmonics. Other possible choices include the atomically centered gaussians or maximally localized Wannier functions (Marzari and Vanderbilt, 1997). As soon as the localized d-orbitals are defined, even the schemes using plane waves as basis sets, such as pseudopotential methods in the DFT can be implemented.

To illustrate the necessity of the Hubbard U correction in predicting the electronic properties of transition metal oxides, the density of states (DOS) of MnO and FeO calculated by LDA and LDA + U are shown in Fig. 3. Here, it can be seen that under the standard LDA, the bandgap for MnO is underestimated, while FeO is incorrectly predicted to have a metallic behavior. This is true for many other transition metal oxides, where the d-electrons hybridize quite strongly with other orbitals while remaining localized.

In the recent years, significant progress into a more robust state-of-the-art approach for strongly correlated systems was driven by the development of dynamical mean-field theory (DMFT). A key insight into this approach is that an infinite lattice could be mapped approximately onto an impurity problem, which must be solved self-consistently (Georges *et al.*, 1996). This is because of the idea that in the limit of infinite dimensions, self-energy becomes local. Hence, it would be possible for techniques developed for impurity models to be used for the Hubbard model. Thus, a natural generalization of the LDA + U scheme for the local dynamical effects is to use the concept of DMFT. In such LDA + DMFT approach, *ab initio* calculations based on an LDA implementation of DFT are first performed to obtain the one-electron part of the Hamiltonian. The high-energy states are then integrated out to construct a basis of first-principles Wannier functions, while retaining only the low-energy partially filled (d or f) bands. These Wannier functions are localized and carry information about the lattice, making the correlation part of the Coulomb repulsion very short range in such basis. Finally, the dynamical mean-field approximation is used to solve the material-specific few-bands many-body Hamiltonian that was expressed in terms of the Wannier functions. Such combined LDA + DMFT approach has been used successfully in understanding the properties of strongly correlated systems, such as the role of subtle crystal-field splitting for the metal-insulator transition in 3dⁿ transition-metal oxides (Pavarini *et al.*, 2004).

In the framework of the LDA + DMFT approach, one rigorous way to solve an effective impurity problem is the Quantum Monte Carlo (QMC) method (Takegahara, 1993; Rozenberg, 1997). In such technique, the interacting electron problem is essentially mapped onto a sum of non-interacting problems, where the particle moves in a fluctuating, time-dependent field. The algorithm then evaluates this sum by Monte Carlo sampling. One advantage of this method is that it is (numerically) exact, which allows the calculation of a one-particle Green's function, as well as two-particle (or higher) Green's functions.

Correlated Oxide Materials

In this section, the applications of the theoretical methods and schemes for correlated systems will be discussed to specific metal oxide materials such in Ti₂O₃, perovskite oxides, superconducting cuprates, and others. As previously mentioned for the case of transition metal oxides, their unique electronic properties stem from the delicate balance between the electron correlation effects and hybridization of orbitals. For a d-d orbital interaction with weak Coulomb correlation, there is a bonding-antibonding splitting of bands when bonds are formed. On the other hand, when the on-site electron-electron interaction is much stronger than d-d hybridization, the wave function will be localized with large renormalization of inter-site hybridization and reduced bonding-antibonding splitting. At such strong Coulomb interaction, chemical bonding is reduced. Likewise, in the limit of a strong bonding-antibonding splitting, the correlation effect is largely reduced.

Poteryaev *et al.* discussed the competition of correlation effects and chemical bonding for the case of Ti₂O₃, whose complicated electronic structure, together with the origin of its metal-insulator transition, is a subject of intensive experimental and theoretical research over the past years (Poteryaev *et al.*, 2004; Imada *et al.*, 1998). A generally accepted explanation for the metal-insulator transition for Ti₂O₃ is the decrease of the c/a ratio in its rhombohedral structure and the formation of a Ti-Ti dimer along z-axis, as

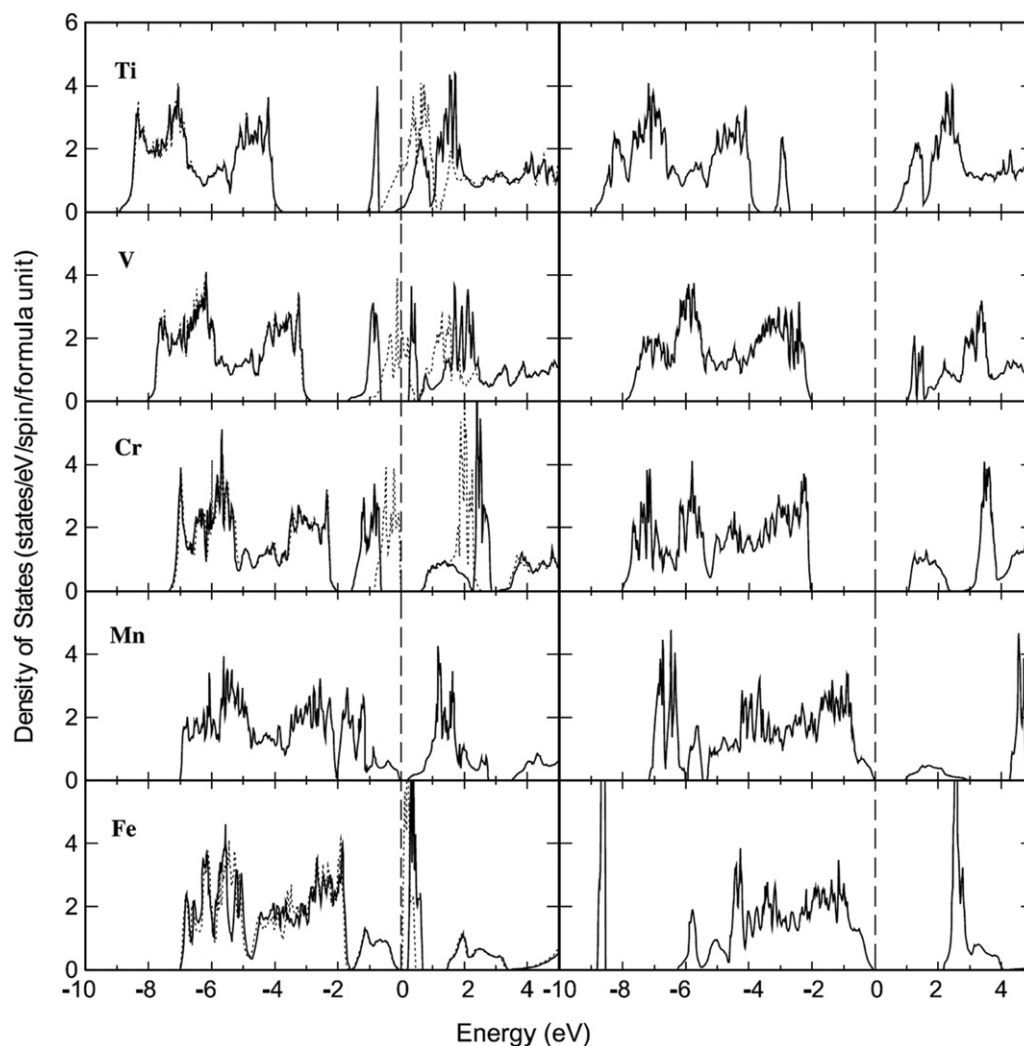


Fig. 5 The left panel shows the density of states of LaMeO_3 calculated using the standard LDA (dotted lines) LDA + U_{t2g} (solid lines), while the right panel shows the results calculated using LDA + U . The zero energy corresponds to the Fermi level. Reprinted with permission from Solovyev, I., Hamada, N., Terakura, K. 1996b. t_{2g} versus all 3d localization in LaMO_3 perovskites ($M = \text{Ti-Cu}$): First-principles study. *Physical Review B* 53, 7158. Copyright 1996 by the American Physical Society.

shown in **Fig. 4** (Goodenough, 1971; Uchida *et al.*, 2008). The metallic and insulating phases of Ti_2O_3 have an $\alpha\text{-Al}_2\text{O}_3$ corundum structure with two formula units per rhombohedral cell (Abrahams, 1963; Rice and Robinson, 1977). A large $t_{2g} - e_g^\sigma$ splitting of orbitals is formed as the Ti atoms are octahedrally surrounded by the oxygen atoms (Poteryaev *et al.*, 2004). An additional splitting of the t_{2g} bands into $e_g^\pi - a_{1g}$ is formed due to a trigonal distortion, while the a_{1g} sub-bands of the Ti-Ti pair form a strong bonding-antibonding counterpart (**Fig. 4**). In principle, an insulating d^1 configuration of Ti_2O_3 can form as the large decrease in the Ti-Ti bond could split even further an occupied single-degenerate a_{1g} state from a double-degenerate e_g^π state of the t_{2g} sub-band. Nevertheless, LDA calculations have shown that Ti_2O_3 remains to be metallic for reasonable distances of the Ti-Ti pair (Mattheiss, 1996). It is also noteworthy to mention that an accurate estimation of the a_{1g} and e_g bandwidths of Ti_2O_3 is required to investigate the role of electron-electron interactions in its insulating low-temperature phase. A drastic underestimation of the a_{1g} and e_g bandwidths can easily produce a gap, as in the case of a cluster mean-field investigation of $[\text{Ti}_2\text{O}_9]^{12-}$ (Nakatsugawa and Iguchi, 1997). Using a cluster DMFT scheme, Poteryaev *et al.* have shown that the small semiconducting gap structure in Ti_2O_3 is due to the competition between strong bonding within the Ti-Ti pair and localization from correlation effects. In this method, a numerically exact multi-orbital Quantum Monte Carlo scheme is employed for the solution of the cluster DMFT, with an accurate first principles tight-binding parametrization for the one electron structure. Their developed strategy first investigates the gap formation using a single site and a cluster LDA + DMFT with only local correlations. A full non-local cluster DMFT was then employed to directly elucidate the impact of non-local Coulomb interactions on the physics of this system. Such result for the semiconducting band gap of Ti_2O_3 illustrates that the non-local Coulomb correlations are important in the study of similar systems with small band gap (Poteryaev *et al.*, 2004).

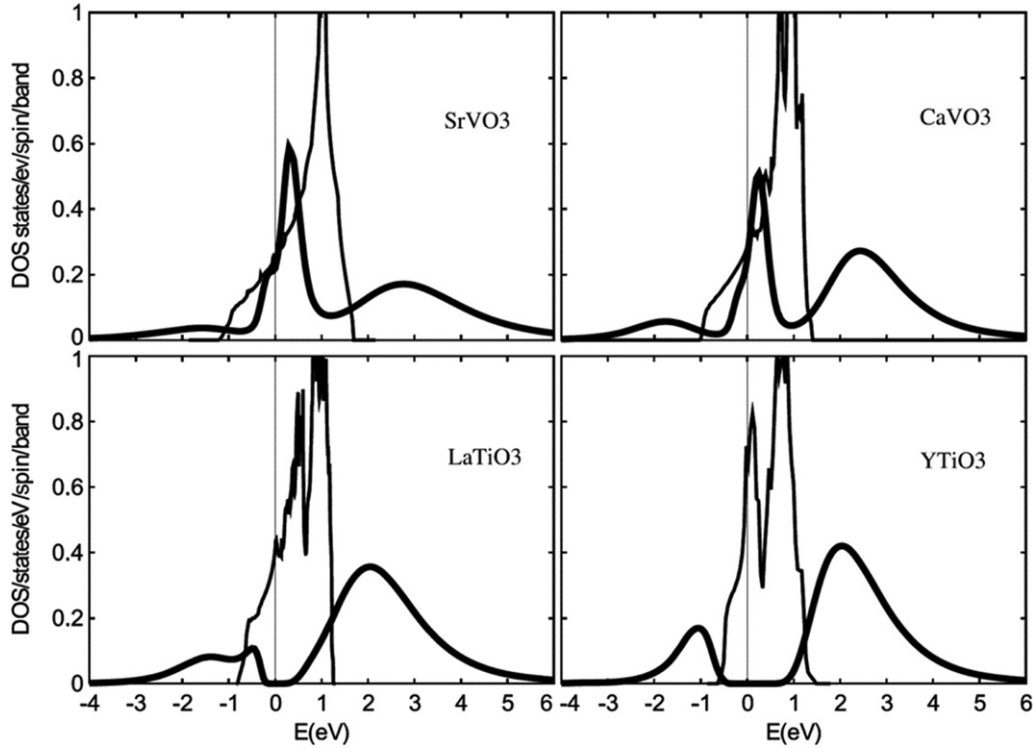


Fig. 6 The LDA + DMFT spectral function (thick line) for different perovskites at $T = 770$ K and the LDA calculated DOS (thin line). Reprinted with permission from Pavarini, E., Biermann, S., Poteryaev, A., *et al.*, 2004. Mott transition and suppression of orbital fluctuations in orthorhombic 3d1 perovskites. *Physical Review Letters* 92, 176403. Copyright 1998 by the American Physical Society

A class of oxide materials that pose very interesting properties is the perovskite. Due to their applications for high temperature superconductor systems and other devices for alternative energy applications, studies on the electronic properties of perovskite oxides have gained much interest in the recent years. In particular, transition metal perovskites have attracted much attention because of their unusual electronic and magnetic properties, which arise from their narrow 3d bands and strong Coulomb correlations. A comparison of the electronic structures of the LaMeO_3 oxides (with $\text{Me} = \text{Ti, V, Cr, Mn, and Fe}$) is shown in Fig. 5, which are calculated using the standard LDA, and LDA + U with two types of the U-corrections. The density of states shown in the left panel corresponds to the U-corrections that are added only to the localized t_{2g} states of the Me^{3+} ion (since the e_g states are much more delocalized in perovskites) (Solovyev *et al.*, 1996b). On the other hand, the right panel shows the density of states calculated using the standard LDA + U scheme with the U-correction applied to all d-states. It can be seen that the results for LDA + $U_{t_{2g}}$ is much closer to the standard LDA since the U-correction to the t_{2g} states has only a very small effect due to the effective screening from e_g states. Nevertheless, both methods underestimate the value of the band gap, unlike the LDA + U method that gives band gap values that are close to the experimental results.

Interestingly, the 3d¹ perovskites may exhibit different properties despite the lack of its multiple structures. For example, SrVO_3 and CaVO_3 are correlated metals, while LaTiO_3 and YTiO_3 are Mott insulators (Imada *et al.*, 1998; Pavarini *et al.*, 2004). To illustrate this, the DMFT spectral functions and the LDA total density of states for these systems are shown in Fig. 6. Here, it can be seen that for the case of cubic SrVO_3 , the lower and upper Hubbard bands are at around -1.8 eV and 3.0 eV, respectively. For the CaVO_3 perovskite, the lower Hubbard band remains at around -1.8 eV while the upper Hubbard band moves to a lower energy of 2.5 eV. These calculations for SrVO_3 and CaVO_3 are in good agreement with photoemission data (Imada *et al.*, 1998), which demonstrate the similar properties of these materials, with the latter being slightly more correlated (Pavarini *et al.*, 2004). For the LaTiO_3 and YTiO_3 perovskites, the lower Hubbard band is at around -1.5 eV, in agreement with a photoemission experiment (Imada *et al.*, 1998). Interestingly, despite their very similar bandwidths ($W = 2.1$ eV and 1.9 eV for LaTiO_3 and YTiO_3 respectively), their band gaps are very different (0.3 eV and 1.0 eV, respectively). This illustrates that the Mott transition and size of the band gap for 3d¹ systems do not depend only on the U/W ratio, but also on the full band structure (Pavarini *et al.*, 2004). LaTiO_3 can generate metallic transport properties when the oxygen stoichiometry (LaTiO_{3+x}) is changed (Okada *et al.*, 1993). Such change in the electronic properties of LaTiO_{3+x} has been reported in phase diagrams, which show its good metallic properties over a wide temperature range at oxygen stoichiometries of $0.1 < x < 0.25$ (Lichtenberg *et al.*, 1991). Also, doping LaTiO_3 with a very small amount of Sr leads to the transition into a paramagnetic metal with a strongly correlated character. A comparison of the experimental photoemission spectrum (Fujimori *et al.*, 1992a,b) with the LDA calculation and LDA + DMFT Quantum Monte Carlo simulation for LaTiO_3 with 6% hole doping has shown that the LDA fails to reproduce the broad band observed in the photoemission experiment at energies of around 1 – 2 eV below the Fermi energy. When a U correction for the electron correlation

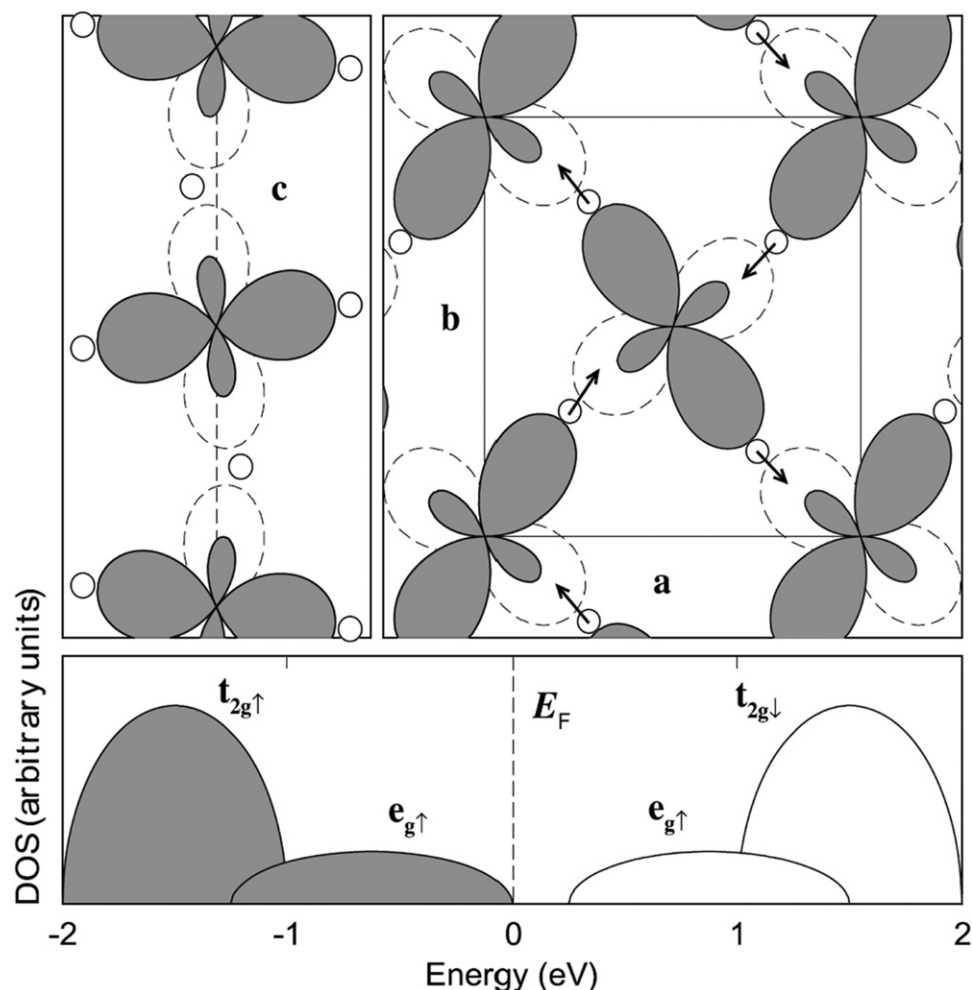


Fig. 7 The upper panel shows the orbital ordering of orthorhombic LaMnO_3 along c axis and in a - b plane. The occupied e_g states of $3x^2-r^2$ and $3z^2-r^2$ symmetry are denoted by shaded orbits, while the empty e_g states of y^2-z^2 and x^2-z^2 symmetry are denoted by broken lines. The lower panel shows a schematic diagram for the positions of the $t_{2g\uparrow}$, $t_{2g\downarrow}$, and $e_{g\uparrow}$ band split by Jahn-Teller distortion in the LDA calculation. Reprinted with permission from Solovyev, I., Hamada, N., Terakura, K., 1996a. Crucial role of the lattice distortion in the magnetism of LaMnO_3 . *Physical Review Letters* 76, 4825. Copyright 1996 by the American Physical Society.

is taken into account, such broad band can be easily identified as the lower Hubbard band, whose spectral weight originates from the quasiparticle band at the Fermi energy and increases with the value of U . A large $U = 5$ eV value gives the best agreement between the simulation and experiment in terms of the relative intensities and positions of the Hubbard bands. It should be noted that the photoemission experiment is sensitive to surface properties. Because of the reduced coordination at the surface, the bandwidth is likely to be smaller, while the Coulomb interaction is larger (as it is less screened). This makes the system more correlated; which explains why a large $U = 5$ eV value results in a better agreement with the experiment. These results clearly show that the LDA + DMFT approach does not only explain the existence of the lower Hubbard band in doped LaTiO_3 , but also reproduces the qualitative picture of the spectral weight transfer from the quasiparticle band to the lower Hubbard band, the position of the lower Hubbard band, and the narrowing of the quasiparticle band.

Another interesting perovskite is LaMnO_3 , which has an insulating ferromagnetic property, in which electrons are localized in atomic orbitals (Coey *et al.*, 1999). When doped with divalent alkali-earth dopants A , such as Sr, Ca, or Ba, the $(\text{La}_{1-x}\text{A}_x)\text{MnO}_3$ perovskite exhibits both metallic and ferromagnetic properties. When the La atoms in such system are replaced by the dopants in the concentration range of $0.2 < x < 0.4$, a double exchange mechanism ($\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$) yields its metallic and ferromagnetic behavior (Zener, 1951). On the other hand, the undoped system has an antiferromagnetic property that corresponds to an Anderson superexchange mechanism. Interestingly, the crystal distortion of manganites has been shown to play an important role in its electronic and magnetic properties, as illustrated in Fig. 7 (Solovyev *et al.*, 1996a). The two principal types of distortion for the LaMnO_3 crystal lattice are the Jahn-Teller distortion (*i.e.*, local tetragonal distortion of the oxygen atoms around the Mn sites) and the orthorhombic superstructure that results from the small tilting of the MnO_6 octahedra. Such crystal distortions appear to be strong enough to split the double degenerate e_g states around the Fermi level as shown in Fig. 7.

Another class of materials that exhibit a perovskite structure is the superconducting cuprate, which is a layered material consisting of superconducting layers of copper oxide. Its pristine (undoped) compound is a Mott insulator with a long-range antiferromagnetic order at sufficiently low temperatures. It can be argued that one of the most interesting discoveries of recent decades is the synthesis of superconducting cuprates such as the LSCO ($\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$), YBCO ($\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$), and BSCCO ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$) (Bednorz and Müller, 1986; Damascelli *et al.*, 2003), whose superconducting mechanism continues to be the subject of considerable debate and ongoing research. For YBCO, the Cu–O chains are identified to have a key role in its superconductivity. A doped YBCO, yttrium-barium cuprate ($\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$) or Y123, was the first superconductor to be found above the boiling point of liquid nitrogen. T_s is maximal near 92 K when $x \approx 0.15$, while its superconducting property disappears at $x \approx 0.15$, as its structure transforms from orthorhombic to tetragonal (Khare, 2003).

Some other perovskites of interest have various applications and noteworthy electronic properties. LaNiO_3 exhibits metallic character because of the charge-transfer gap Δ closing, as manifested by the overlap of the occupied oxygen 2p and unoccupied 3d Ni orbitals. Interestingly, its oxygen-deficient phase (LaNiO_{3-x}) has been observed to have a metal-to-insulator transition, which implies the importance of controlling the oxygen stoichiometry (Sanchez *et al.*, 1996). The perovskite SrRuO_3 has a metallic property due to the overlap of the oxygen anion p and cation t_{2g} orbitals (Callaghan *et al.*, 1966). The perovskite LaCoO_3 is a charge-transfer insulator with band gap characterized by the occupied oxygen 2p band and an unoccupied cobalt 3d e_g band (Norton, 2004). When it is doped with a cation, such as in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, the $\text{Co}^{3+}/\text{Co}^{4+}$ valency ratio increases, which yields a metallic behavior. In such system, the oxygen stoichiometry is crucial as it can change the $\text{Co}^{3+}/\text{Co}^{4+}$ valency ratio and the structural disorder in the Co–O–Co conduction channel (Prokhorov *et al.*, 2002). These perovskites continue to be relevant in the research and development of materials for the future.

Conclusion

This article discussed the electronic properties of complex oxides, with emphasis on the role of the strong Coulomb interaction in its unique electronic and magnetic properties. While the local density approximation is a reasonable method for the electronic structure studies of metallic oxides, an additional Hubbard-like correction is important for oxides with insulating properties. The strong Coulomb interaction for oxides with insulating properties is enough to cause the localization of electrons, which yields a band gap in its electronic structure. The LDA + U method is demonstrated to be efficient and reliable in investigating the electronic structures of such insulating oxides such as in transition metal oxides, where the 3d-orbitals hybridize strongly with the oxygen p-orbitals. The main advantage of such method over model approaches to many-body problems is its *ab initio* nature that requires no empirical parameters. However, the LDA + U method overestimates the tendency of electrons to localize, as is similarly noted for the Hartree-Fock type approach. Improvements to the LDA + U include the dynamical character of the effective potential acting on electrons, where the Green's function is solved instead of the density matrix, and with self-energy term instead of the effective exchange-correlation potential. Such LDA + DMFT method is a state-of-the-art approach in describing materials with strong electron correlation, which provides an opportunity to unify the many-body theory with the *ab initio* calculations of the electronic properties of materials. The applications of these methods to specific materials such as perovskites, cuprates, and other transition metals were discussed in relation to their various technological and scientific significance. The study of these materials will continue to be an exciting endeavor in materials science.

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Ionic Conductivity

Steffen Neitzel-Grieshammer, Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

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Abstract

Ionic conductivity is a fundamental property of oxide materials that is utilized in applications such as fuel cells, batteries, and gas sensors. The ionic conductivity is directly linked to the motion of defects in the oxide lattice. In this article, the fundamentals of defect chemistry and mobility of defects are discussed and exemplified for the well-known oxygen ion conductor cerium oxide. In the end, the reader will understand the formation of defects, calculation of defect concentrations, migration mechanisms and the connection to the macroscopic transport of ions.

Key Points

- Introduction to point defect chemistry.
- Role of concentration and mobility for conductivity.
- Formation mechanisms of defects.
- Microscopic and macroscopic effects on ionic conductivity.
- Dependence of defects fraction on temperature and partial pressure.

Introduction

Ionic conductivity is, without doubt, one of the most important and interesting properties of functional solid state oxides. The ability of the materials to conduct electrical current by ions is decisive for the effectiveness of electrolytes and electrodes in batteries and fuel cells, fundamental for sensors, and plays an important part in material degradation.

For example, the lambda probe, designed to measure the exhaust-gas concentration of oxygen for internal combustion engines, is a component of almost any vehicle and relies on a solid state ion conductor.

Nowadays, the shift to energies from renewable sources and the extension of electric mobility demands the availability of electrochemical energy storage systems where solids with high ionic conductivity are crucial.

Solid state materials in general, and oxides in particular, are generally not regarded as good ionic conductors. In contrast, some oxides, such as lithium ion and sodium ion conductors, show surprisingly high ionic conductivity that can compete with or even exceed the conductivity of liquid electrolytes as found in state-of-the-art lithium ion batteries (Meesala *et al.*, 2017).

From a structural point of view, solid state materials can be separated into two main groups: amorphous and crystalline. Amorphous solids only exhibit a local ordering while no long range order exists similar to a liquid. Although there are examples of amorphous ionic conductors, we here focus on ionic conductivity in crystalline solids that are characterized by their translational invariance: An irreducible unit cell is multiplied in each spatial direction and the structure is exactly the same when moving along the lattice vectors. In a perfect crystal, no ionic motion would be possible as the ions stick to their individual positions. However, real crystals contain defects on the microscopic level that enable the transport of ions.

One of the earliest prominent examples of an ion conducting oxide is substituted zirconia (ZrO_2). Several percent of the zirconium ions are replaced by lower valent cations such as yttrium in the composition $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-x/2}$ known as yttria-stabilized zirconia (YSZ). As suggested by the molecular formula, the introduction of yttrium ions lowers the oxygen content, thus introducing oxygen vacancies in the zirconia structure that enable the ionic transport. YSZ was applied first in 1897 by Walther Nernst in an early type of an incandescent lamp, the so-called Nernst lamp (Mills, 2013). In contrast to lamps with carbon or metal filaments a ceramic rod was used as the light source, that was not oxidized in air atmosphere, thus no vacuum environment was required. Now it has been more than 100 years since the introduction of this application and the Nernst lamp has long been replaced by more efficient and convenient light bulbs and light emitting diodes. Nevertheless, YSZ remains an important electrolyte material in fuel cells and oxygen sensors, combining high ionic conductivity with chemical stability and low electronic conductivity.

In general, the total conductivity σ_{total} of a solid oxide is the sum of its ionic (σ_{ion}) and electronic (σ_{elec}) conductivity. The electronic charge carriers include electrons and electron holes while all ions can contribute to the ionic conductivity:

$$\sigma_{\text{total}} = \sum_i \sigma_i = \sum_i \sigma_{\text{ion},i} + \sum_i \sigma_{\text{elec},i} \quad (1.1)$$

However, for most materials, the partial conductivities vary by orders of magnitude, and the total conductivity is often determined by only one mobile species while the others are regarded as immobile. These variations could be due to differences in the concentration of the respective charge carriers c with charge q or their mobility μ according to

$$\sigma_i = c_i \cdot q_i \cdot \mu_i. \quad (1.2)$$

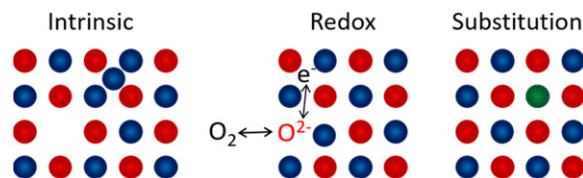


Fig. 1 Illustration of different mechanisms of defect formation. Intrinsic defect disorder (left), oxygen exchange with the atmosphere (center) and substitution (right). Cations are depicted in blue and oxygen ions in red.

As the transport of ions in a crystalline solid is only possible by defects and the defect concentration is crucial for the ionic conductivity, we will focus on defects and their formation mechanisms in the next section before turning to mobility of the defects and the ionic conductivity in solids.

This article was written based on the long experience of the author in the field of ionic conductivity in oxide materials. Furthermore, if not mentioned otherwise, the following excellent books were consulted and are suggested for further information: (Chiang *et al.*, 1997; Howard and Lidiard, 1964, Maier, 2004, Waser and Ielmini, 2016).

Concentration of Defects in Oxides

The mobile defects in a crystalline solid can be either vacancies, representing an empty lattice site that is occupied in the ideal structure, or an interstitial, where a new – non-regular site – site is occupied.

For a concise representation of defects and regular lattice elements, the Kröger-Vink notation was introduced (Kröger and Vink, 1956). This combines three information: The type of element (S), the lattice site (L) and its relative charge (ε) such that each lattice element is written as S_L^ε . S is either the respective element symbol or a V or v denoting a vacancy. L is the lattice site denoted by the element symbol occupying the respective site in the ideal structure. In addition, an interstitial is denoted by the letter I or i . The charge $\varepsilon = z_{\text{real}} - z_{\text{ideal}}$ is given relative to the charge of the ideal occupation. An oxygen vacancy would thus have the relative charge of $0 - (-2) = 2$. To distinguish the relative charges from absolute charges, new symbols are introduced: The $'$ denotes a negative charge, $\bullet$ a positive charge, and $\times$ represents a relative charge of zero. Higher charges are expressed by multiplying these symbols. An oxygen vacancy is thus written as $V_O^{\bullet\bullet}$, an oxygen interstitial as $O_i^{'}$ and an yttrium ion on a cerium site is given by $Y_{Ce}^{\times}$.

The Kröger-Vink notation summarizes the information required to define a defect and already suggests the constraints in defect chemistry. Conservation of mass and charge are well known to all chemists, stating that atoms and charges cannot be generated or destroyed during a chemical reaction. In defect chemistry, a further constraint is the conservation of lattice sites. Admittedly, lattice sites can be generated or destroyed, but only in stoichiometric ratio. Thus, it is impossible to generate only Ce-sites in ceria (CeO_2) but it is possible to generate one Ce-site accompanied by two O-sites.

In ionic crystals, defects are usually charged and thus negative defects are accompanied by positive defects to satisfy the charge neutrality condition accounting for the relative charge ε_i and concentration c_i of the defects:

$$\sum_i \varepsilon_i c_i = 0 \quad (2.1)$$

The concentration of defects can vary by orders of magnitude with three major types of mechanisms determining the concentration as illustrated in Fig. 1. At temperatures above absolute zero, intrinsic defects are formed by thermal excitation. In addition, the exchange with another phase can lead to the formation of defects. In oxides, the typical example is the exchange of oxygen with the surrounding atmosphere, leading to a release of oxygen under reducing conditions and uptake of oxygen under oxidizing conditions. In addition, deliberate variation of the defect concentration is possible by doping or substitution.

Intrinsic Defect Formation

Above absolute zero, defects are formed by thermal excitation. As the charge neutrality condition (Eq. (2.1)) has to be maintained, defects of opposite charge are formed for compensation. Considering the formation of vacancies and interstitials, three types of intrinsic defect disorders are defined. These are exemplified for ceria in Eqs. (2.2)–(2.4) and illustrated in Fig. 2.

- Frenkel disorder: A cation is displaced from its regular position to an interstitial site, leaving a cation vacancy behind:



- Anti-Frenkel disorder: An anion is displaced from its regular position to an interstitial site, leaving an anion vacancy behind:



- Schottky disorder: Anions and cations in stoichiometric ratio move to the surface leaving the corresponding vacancies behind:

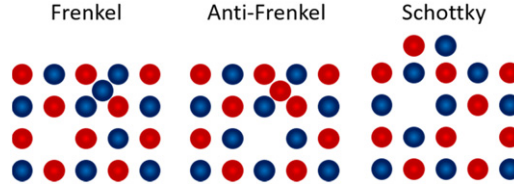


Fig. 2 Illustration of intrinsic disorder in an ionic crystal AO. Frenkel (left), anti-Frenkel (center), Schottky (right). Cations are depicted in blue and oxygen ions in red.



An inverted Schottky disorder, where ions leave the surface to form interstitials could be expressed by a combination of the three types of disorder shown above.

While the formation of each individual defect pair is endergonic, the formation of the intrinsic defects is driven by the increase of the configurational entropy ΔS_{c} of the lattice. For Frenkel disorder, the total Gibbs energy of the lattice G_{lattice} can be expressed by

$$G_{\text{lattice}} = G_{\text{ideal}} + G_{\text{defects}} = G_{\text{ideal}} + N_{\text{F}}\Delta g_{\text{F}} - T\Delta S_{\text{c}}. \quad (2.5)$$

Here, G_{ideal} is the Gibbs energy of the lattice without defects. The change of Gibbs energy due to defect formation G_{defects} includes two contributions: $\Delta g_{\text{F}} = \Delta h_{\text{F}} - T\Delta s_{\text{F}}$ is the Gibbs energy required to form a Frenkel pair (cation vacancy and interstitial), with the enthalpy Δh_{F} and the non-configurational entropy Δs_{F} . The configurational entropy results from Boltzmann's equation $\Delta S_{\text{c}} = k_{\text{B}}\ln(\Omega)$ with the number of possible configurations Ω .

For simplicity we consider in the following a crystal of composition AO and assume that the total number of cation sites N equals the total number of possible interstitial sites. The charge neutrality condition for Frenkel disorder is given by $N_{\text{V}} = N_{\text{i}} = N_{\text{F}}$, where N_{V} denotes the number of cation vacancies and N_{i} the number interstitial ions which is equal to the number of Frenkel pairs N_{F} according the reaction



For the cation sublattice, the number of possible arrangements Ω can be calculated by

$$\Omega = \frac{N!}{(N - N_{\text{F}})!N_{\text{F}}!}. \quad (2.7)$$

We get the same result for the interstitial sublattice and thus the configurational entropy is given by

$$\Delta S_{\text{c}} = 2k_{\text{B}}\ln\left(\frac{N!}{(N - N_{\text{F}})!N_{\text{F}}!}\right). \quad (2.8)$$

and the change of the Gibbs energy due to Frenkel disorder is

$$G_{\text{defects}} = N_{\text{F}}\Delta g_{\text{F}} - 2k_{\text{B}}T\ln\left(\frac{N!}{(N - N_{\text{F}})!N_{\text{F}}!}\right). \quad (2.9)$$

Since the numbers N and N_{F} are large for macroscopic crystals, we can apply Stirling's approximation $\ln(N!) = N\ln(N) - N$ and simplify Eq. (2.9) to

$$G_{\text{defects}} = N_{\text{F}}\Delta g_{\text{F}} - 2k_{\text{B}}T\left[N\ln\left(\frac{N}{N - N_{\text{F}}}\right) + N_{\text{F}}\ln\left(\frac{N - N_{\text{F}}}{N_{\text{F}}}\right)\right]. \quad (2.10)$$

To find the equilibrium number of Frenkel defects we now have to minimize G_{defects} with respect to N_{F} according to

$$\frac{\partial G_{\text{defects}}}{\partial N_{\text{F}}} = \Delta g_{\text{F}} + 2k_{\text{B}}T\ln\left(\frac{N_{\text{F}}}{N - N_{\text{F}}}\right) \equiv 0. \quad (2.11)$$

By rearranging we find the site fraction $n_{\text{F}} = \frac{N_{\text{F}}}{N}$ of the Frenkel defects with

$$n_{\text{F}} \approx \frac{N_{\text{F}}}{N - N_{\text{F}}} = \exp\left(-\frac{\Delta g_{\text{F}}}{2k_{\text{B}}T}\right). \quad (2.12)$$

Alternatively, we can define the molar fraction of defects [*defect*] as the number of defects per formula unit. For perfect ceria we would thus have $[\text{Ce}_{\text{Ce}}^{\times}] = 1$ and $[\text{O}_{\text{O}}^{\times}] = 2$. Another useful definition is the concentration of defects c_{defect} , given per m^3 or cm^3 , that is the molar fraction divided by the molar volume.

From a classical chemical point of view we can apply the mass action law to Eq. (2.6):

$$K_{\text{F}} = \frac{[\text{V}_{\text{A}}^{\prime\prime}][\text{A}_{\text{i}}^{\bullet\bullet}]}{[\text{A}_{\text{A}}^{\times}][\text{V}_{\text{i}}^{\times}]} = \exp\left(-\frac{\Delta g_{\text{F}}}{k_{\text{B}}T}\right) \quad (2.13)$$

As the defect fraction is small, we can approximate the molar fraction of the regular lattice elements in our example by $[\text{A}_{\text{A}}^{\times}] = [\text{V}_{\text{i}}^{\times}] = 1$. With the charge neutrality condition we then obtain

Table 1 Energies and entropies of intrinsic defect formation in ceria calculated by density functional theory and defect fractions at 500°C for each individual equilibrium

Type of disorder	$\Delta E/\text{eV}$	$\Delta S/k_B$	[defect pairs]
Frenkel	12.46	10.5	4.7×10^{-39}
Anti-Frenkel	4.14	5.0	5.6×10^{-13}
Schottky	6.87	4.5	5.3×10^{-15}

Note: Zacherle, T., Schriever, A., Souza, R., Martin, M., 2013. *Ab initio* analysis of the defect structure of ceria. Physical Review B 87, 134104. Grieshammer, S., Zacherle, T., Martin, M., 2013. Entropies of defect formation in ceria from first principles. Physical Chemistry Chemical Physics 15, 15935. Martin, M., Zacherle, T., Schriever, A., Souza, R.A., Grieshammer, S., 2013. *Ab initio* calculation of the defect structure of ceria. ECS Transactions 57, 2405–2410.

$$[V_A''] = [A_i^{\bullet\bullet}] = \exp\left(-\frac{\Delta g_F}{2k_B T}\right). \quad (2.14)$$

Eq. (2.14) is equivalent to Eq. (2.12) and consequently we can extend the classical mass action law to defect reactions. This result is independent of the aforementioned assumptions and the type of defect disorder. Analogously, we obtain the mass action laws for anti-Frenkel and Schottky disorder:

$$K_{AF} = \frac{[O_i''] [V_O^{\bullet\bullet}]}{[O_O^{\times}] [V_i^{\times}]} = \exp\left(-\frac{\Delta g_{AF}}{k_B T}\right) \quad (2.15)$$

$$K_S = \frac{[V_A'] [V_O^{\bullet\bullet}] a_{AO}}{[O_O^{\times}] [A_A^{\times}]} = \exp\left(-\frac{\Delta g_S}{k_B T}\right) \quad (2.16)$$

Here a_{AO} is the activity of the newly formed AO phase at the surface.

We now apply this approach to our example of ceria according to Eqs. (2.2)–(2.4) and combine these with the respective charge neutrality conditions to obtain the individual molar fractions of defects:

$$[Ce_i^{\bullet\bullet\bullet}] = [V_{Ce}'''] = ([Ce_{Ce}^{\times}] [V_i^{\times}])^{1/2} \exp\left(-\frac{\Delta g_F}{2k_B T}\right) \approx K_F^{1/2} \quad (2.17)$$

$$[V_O^{\bullet\bullet}] = [O_i''] = ([O_O^{\times}] [V_i^{\times}])^{1/2} \exp\left(-\frac{\Delta g_{AF}}{2k_B T}\right) \approx (2K_{AF})^{1/2} \quad (2.18)$$

$$[V_O^{\bullet\bullet}] = 2[V_{Ce}'''] = 2\left(\frac{[Ce_{Ce}^{\times}] [O_O^{\times}]^2}{4a_{CeO_2}}\right)^{1/3} \exp\left(-\frac{\Delta g_S}{3k_B T}\right) \approx 2K_S^{1/3} \quad (2.19)$$

Here, we assumed $[Ce_{Ce}^{\times}] = [V_i^{\times}] \approx 1$, $[O_O^{\times}] \approx 2$ and $a_{CeO_2} \approx 1$ for the newly formed pure CeO_2 phase. Table 1 presents the energies and entropies of intrinsic defect formation in ceria calculated by density functional theory (Zacherle *et al.*, 2013, Grieshammer *et al.*, 2013, Martin *et al.*, 2013). In addition, the molar fraction of defect pairs calculated at 500°C is given according to Eqs. (2.17)–(2.19) approximating the enthalpy of formation Δh with the energy of formation ΔE . From the presented data it is clear, that the fractions of defects vary by orders of magnitude. In the present case, Anti-Frenkel disorder is favored over Schottky disorder, whereas the effect of Frenkel disorder is negligible.

Generally, the predominant type of disorder in a crystal with a certain structure and composition is not known without experimental or computational evidence. Nevertheless, there are some presumptions possible based on the structure and ionic radii. For example, the formation of interstitials is not favorable in close-packed structures and Schottky disorder can be expected to be dominant. Nevertheless, we generally have to solve Eqs. (2.17)–(2.19) simultaneously under the restriction of the charge neutrality condition

$$[V_A''] + [O_i''] = [V_O^{\bullet\bullet}] + [A_i^{\bullet\bullet}]. \quad (2.20)$$

A simple analytical solutions of this set of equations cannot be expected. Instead, we can use the so-called Brouwer-approximation assuming that one of the disorder types is much more likely and thus dominates the defect chemistry. As an example we assume that Frenkel disorder is dominating. Thus, $[V_A'']$, $[A_i^{\bullet\bullet}] \gg [V_O^{\bullet\bullet}]$, $[O_i'']$ with the majority defects $[V_A'']$ and $[A_i^{\bullet\bullet}]$ and the minority defects $[V_O^{\bullet\bullet}]$ and $[O_i'']$. The charge neutrality condition then simplifies to $[V_A''] \approx [A_i^{\bullet\bullet}]$.

Now we can calculate the fraction of the Frenkel defects $[V_A'']$ and $[A_i^{\bullet\bullet}]$ according to (2.14) while we obtain the following expressions for $[V_O^{\bullet\bullet}]$

$$[V_O^{\bullet\bullet}] = \frac{K_S}{[V_A'']} = K_S \exp\left(\frac{\Delta g_F}{2k_B T}\right) \quad (2.21)$$

and $[O_i'']$

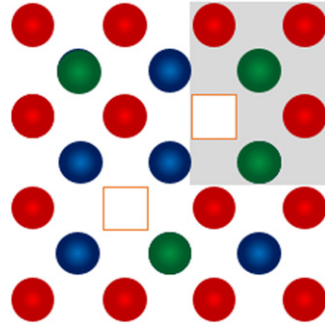


Fig. 3 Illustration of substituting two Y_2O_3 units in a CeO_2 lattice with the formation of Y'_{Ce} and $\text{V}_{\text{O}}^{\bullet\bullet}$. Cerium depicted in blue, oxygen in red and yttrium in green. The gray rectangle illustrates one Y_2O_3 unit in the CeO_2 lattice while the other one is dissolved in the lattice.

$$[\text{O}_i''] = \frac{K_{\text{AF}}}{[\text{V}_{\text{O}}^{\bullet\bullet}]} = \frac{K_{\text{AF}}}{K_{\text{S}}} \exp\left(-\frac{\Delta g_{\text{F}}}{2k_{\text{B}}T}\right). \quad (2.22)$$

Redox Reactions

At sufficiently high temperature, a crystal is in equilibrium with its environment. In particular, oxides exchange oxygen with the atmosphere. Under reducing conditions many oxides tend to form oxygen vacancies and electrons according to



The equilibrium of the redox reaction depends on the activity of oxygen according to

$$K_{\text{R}} = \frac{[\text{V}_{\text{O}}^{\bullet\bullet}][\text{e}']^2}{[\text{O}_{\text{O}}^{\times}]} a_{\text{O}_2}^{1/2}. \quad (2.24)$$

In ceria, the formed electrons are not delocalized over the conduction band but localize as small polarons at the cerium ions, turning $\text{Ce}_{\text{Ce}}^{\times}$ to Ce'_{Ce} . The overall reduction of ceria can thus be written as:



Approximating the activity of oxygen by the oxygen partial pressure divided by the standard pressure p^0 results in:

$$K_{\text{R}} = \frac{[\text{V}_{\text{O}}^{\bullet\bullet}][\text{Ce}'_{\text{Ce}}]^2}{[\text{O}_{\text{O}}^{\times}][\text{Ce}_{\text{Ce}}^{\times}]^2} \left(\frac{p_{\text{O}_2}}{p^0}\right)^{1/2} \quad (2.26)$$

In contrast, at high oxygen partial pressures the lattice is oxidized and could lead to the formation of oxygen interstitials compensated by electron holes:



$$K_{\text{O}} = \frac{[\text{O}_i''][\text{h}^{\bullet}]^2}{[\text{V}_{\text{O}}^{\times}]} a_{\text{O}_2}^{-1/2} \quad (2.28)$$

In addition, the concentration of electrons (in the conduction band) and holes (in the valence band) is connected by the excitation reaction of electrons



with the mass action law

$$K_{\text{e}} = [\text{h}^{\bullet}][\text{e}']. \quad (2.28'')$$

Under redox conditions the material is no longer stoichiometric. The charge neutrality is not ensured by the ionic defects alone and for the electronic defects $[\text{h}^{\bullet}] \neq [\text{e}']$ holds true. The non-stoichiometry is represented by δ such as in $\text{CeO}_{2-\delta}$. When $\delta > 0$, there is an oxygen deficiency and when $\delta < 0$, there is an oxygen excess. It is noted that from the non-stoichiometry we cannot deduce the type of defects. Oxygen deficiency could be due to oxygen vacancies, but also to cation interstitials.

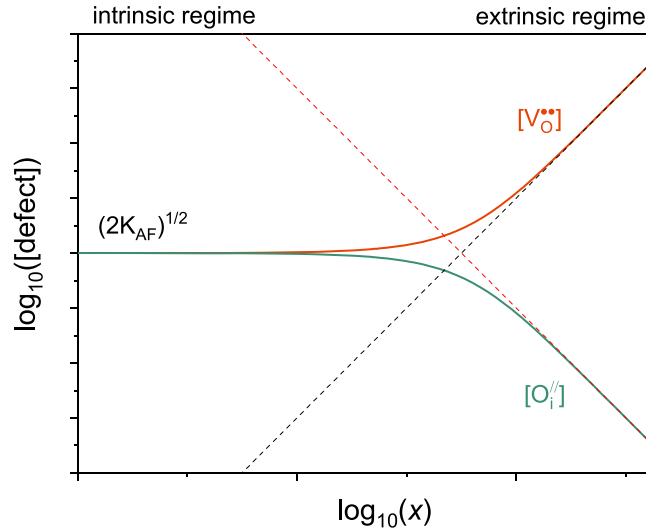


Fig. 4 Illustration of the defect fraction in doped ceria depending on the dopant fraction x . Dashed lines show the approximation in the extrinsic regime.

Substitution

New defects can be created by substitution – also referred to as doping in the case of low concentrations – with another material. In this context, aliovalent substitution is especially interesting as the charge neutrality condition demands the creation of oppositely charged defects. A classical example is the substitution of zirconia or ceria with yttrium oxide. The incorporation of Y_2O_3 leads to the formation of yttrium ions on cerium positions and charge compensating oxygen vacancies with the charge neutrality condition $[Y'_{Ce}] = 2[V_O^{••}]$ as depicted in **Fig. 3**:



In fact, different doping mechanisms are conceivable and **Eq. (2.29)** is not the only possibility. Yttrium ions could also occupy interstitial sites ($Y_i^{•••}$) and various defects are possible for charge compensation including $O_i^{''}$ and $V_{Ce}^{'''}$. While structural aspects and charge differences might give a first indication, experimental or computational evidence is required to identify the pre-dominant mechanism.

Doping allows specific modification of the defect chemistry. However, intrinsic defects are still present. As an example, we consider the effect of doping on the defects in anti-Frenkel disordered ceria. In this case, the charge neutrality condition is given by

$$[Y'_{Ce}] + 2[O_i^{''}] = 2[V_O^{••}] \quad (2.30)$$

At high substitution levels, defect chemistry is dominated by the substitution with the majority defects Y'_{Ce} and $V_O^{••}$ and the minority defects $O_i^{''}$. Thus, **Eq. (2.30)** reduces to $[Y'_{Ce}] = 2[V_O^{••}] = x$ with the dopant fraction x in $Ce_{1-x}Y_xO_{2-x/2}$. Following **Eq. (2.18)**, the fraction of interstitials in this extrinsic regime is given by

$$[O_i^{''}] = \frac{4K_{AF}}{x}. \quad (2.31)$$

At low doping levels, defect chemistry is dominated by intrinsic disorder and the simplified charge neutrality condition in the intrinsic regime is again

$$[O_i^{''}] = [V_O^{••}] = (2K_{AF})^{1/2}. \quad (2.32)$$

For intermediate doping levels we have to combine **Eqs. (2.18)** and **(2.30)** to obtain

$$x + \frac{4K_{AF}}{[V_O^{••}]} = [V_O^{••}]. \quad (2.33)$$

Solving for the molar fraction of oxygen vacancies results in

$$[V_O^{••}] = \frac{x}{2} + \sqrt{\frac{x^2}{4} + 4K_{AF}}. \quad (2.34)$$

Fig. 4 illustrates the relation between the doping level and the molar fraction of the oxygen ion defects. In the limiting cases of intrinsic and extrinsic regime, the defect fractions can be well described by the respective equations as introduced above.

Kröger-Vink-Diagram

In the previous sections we have introduced intrinsic disorder, redox reactions, and substitution to generate defects in the lattice. In real materials, we have a coupled equilibrium of all these reactions whereby the respective defect fractions can vary by orders of magnitude. We are now interested in the dependence of the various defect fractions on the oxygen partial pressure for a given temperature. For our example of doped ceria we have to consider Frenkel disorder (Eq. (2.17)), anti-Frenkel disorder (Eq. (2.18)), Schottky disorder (Eq. (2.19)), and the redox reactions (Eqs. (2.26) and (2.28)). Furthermore, we have to consider the dopant fraction $[Y'_{Ce}] = x$ and the charge neutrality condition including electrons and holes regardless of their (de-)localization:

$$[Y'_{Ce}] + 2[O_i''] + 4[V_{Ce}'''] + [e'] = 2[V_O^{\bullet\bullet}] + 4[Ce_i^{\bullet\bullet\bullet}] + [h\bullet]$$

Solving this set of equations analytically is rather complicated and interpretation of possible solutions would not be very intuitive. Nevertheless, we can apply the Brouwer-approximation for different ranges of the oxygen partial pressure, thus defining the expected majority and minority defects for each range, simplifying the charge neutrality condition to two types of defects. In our example, we define four different ranges for the partial pressure. We know that cation defects are very unlikely, thus the dominating defects are anion defects along with electronic defects and the dopant leading to the following set:

- (1) Low partial pressure $[e'] = 2[V_O^{\bullet\bullet}]$
- (2) Intermediate partial pressure $[Y'_{Ce}] = 2[V_O^{\bullet\bullet}]$
- (3) High partial pressure $[Y'_{Ce}] = [h\bullet]$
- (4) Extremely high partial pressure $2[O_i''] = [h\bullet]$

The problem of solving the coupled defect equilibrium is simplified by solving the equations sequentially for every range of oxygen partial pressure.

- (1) Low partial pressure

We can substitute the charge neutrality condition $[e'] = 2[V_O^{\bullet\bullet}]$ in the mass action law for reduction (Eq. (2.26)) resulting in

$$[e'] = 2[V_O^{\bullet\bullet}] = 2\left(\frac{K_R}{2}\right)^{1/3} a_{O_2}^{-1/6} \quad (2.35)$$

With the fraction of oxygen vacancies we obtain the fraction of oxygen interstitials from anti-Frenkel equilibrium (Eq. (2.18))

$$[O_i''] = \frac{2K_{AF}}{[V_O^{\bullet\bullet}]} = 2K_{AF}\left(\frac{K_R}{2}\right)^{-1/3} a_{O_2}^{1/6} \quad (2.36)$$

and the fraction of cerium vacancies from Schottky equilibrium (Eq. (2.19))

$$[V_{Ce}'''] = \frac{4K_S}{[V_O^{\bullet\bullet}]^2 a_{CeO_2}} = 4K_S\left(\frac{K_R}{2}\right)^{-2/3} a_{O_2}^{1/3}. \quad (2.37)$$

From the latter one we obtain the fraction of cerium interstitials due to Frenkel equilibrium (Eq. (2.17))

$$[Ce_i^{\bullet\bullet\bullet}] = \frac{K_F}{[V_{Ce}''']} = \frac{K_F}{4K_S}\left(\frac{K_R}{2}\right)^{2/3} a_{O_2}^{-1/3}. \quad (2.38)$$

Finally, the fraction of electron holes is set by the excitation equilibrium of electrons:

$$[h\bullet] = \frac{K_e}{[e']} = \frac{K_e}{2}\left(\frac{K_R}{2}\right)^{-1/3} a_{O_2}^{1/6} \quad (2.39)$$

- (2) Intermediate partial pressure

The fraction of oxygen vacancies is set by the doping level $[Y'_{Ce}] = 2[V_O^{\bullet\bullet}] = x$. Accordingly, we can calculate the molar fractions of the other types of defects:

$$[e'] = \left(\frac{2K_R}{[V_O^{\bullet\bullet}]}\right)^{1/2} a_{O_2}^{-1/4} = \left(\frac{4K_R}{x}\right)^{1/2} a_{O_2}^{-1/4} \quad (2.40)$$

$$[O_i''] = \frac{2K_{AF}}{[V_O^{\bullet\bullet}]} = \frac{4K_{AF}}{x} a_{O_2}^0 \quad (2.41)$$

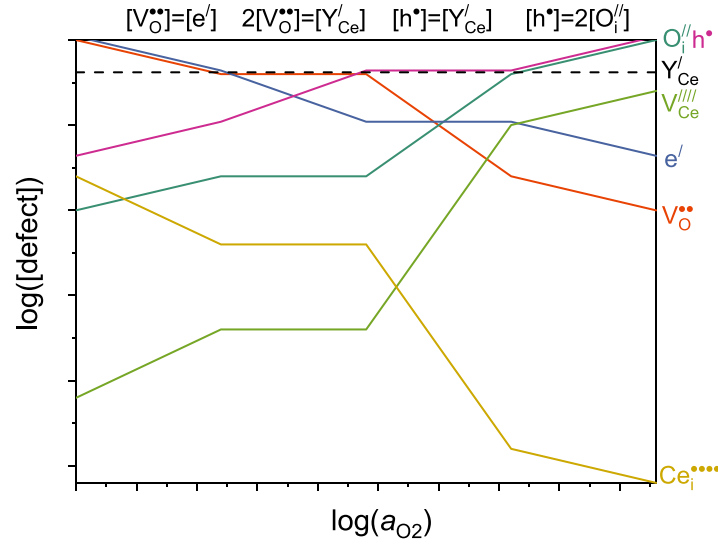


Fig. 5 Schematic Kröger-Vink diagram of doped ceria.

$$[V_{Ce}'''] = \frac{4K_S}{[V_O^{..}]^2 a_{CeO_2}} = \frac{16K_S}{x^2} a_{O_2}^0 \quad (2.42)$$

$$[Ce_i^{....}] = \frac{K_F}{[V_{Ce}''']} = \frac{K_F}{16K_S} x^2 a_{O_2}^0 \quad (2.43)$$

$$[h^{\bullet}] = \frac{K_e}{[e']} = K_e \left(\frac{4K_R}{x} \right)^{-1/2} a_{O_2}^{1/4} \quad (2.44)$$

(3) High partial pressure

As the lattice is oxidized and the oxygen vacancies are filled, the dopant ions are compensated by electron holes $[Y_{Ce}'] = [h^{\bullet}] = x$. For all other defects we obtain the following expressions:

$$[e'] = \frac{K_e}{[h^{\bullet}]} = \frac{K_e}{x} a_{O_2}^0 \quad (2.45)$$

$$[V_O^{..}] = \frac{2K_R}{[e']^2} a_{O_2}^{-1/2} = \frac{2K_R x^2}{K_e^2} a_{O_2}^{-1/2} \quad (2.46)$$

$$[O_i''] = \frac{2K_{AF}}{[V_O^{..}]} = \frac{2K_{AF} K_e^2}{2K_R x^2} a_{O_2}^{1/2} \quad (2.47)$$

$$[V_{Ce}'''] = \frac{4K_S}{[V_O^{..}]^2 a_{CeO_2}} = \frac{4K_S K_e^4}{4K_R x^4} a_{O_2}^1 \quad (2.48)$$

$$[Ce_i^{....}] = \frac{K_F}{[V_{Ce}''']} = \frac{4K_R K_F x^4}{4K_S K_e^4} a_{O_2}^{-1} \quad (2.49)$$

(4) Extremely high partial pressure

Further increase of the oxygen partial pressure results in the formation of oxygen interstitials with $2[O_i''] = [h^{\bullet}]$. We obtain the following expressions for the molar fractions:

$$2[O_i''] = [h^{\bullet}] = 2 \left(\frac{K_O}{4} \right)^{1/3} a_{O_2}^{1/6} \quad (2.50)$$

$$[e'] = \frac{K_e}{[h^{\bullet}]} = \frac{K_e}{2} \left(\frac{K_O}{4} \right)^{-1/3} a_{O_2}^{-1/6} \quad (2.51)$$

$$[V_O^{..}] = \frac{2K_{AF}}{[O_i'']} = 2K_{AF} \left(\frac{K_O}{4} \right)^{-1/3} a_{O_2}^{-1/6} \quad (2.52)$$

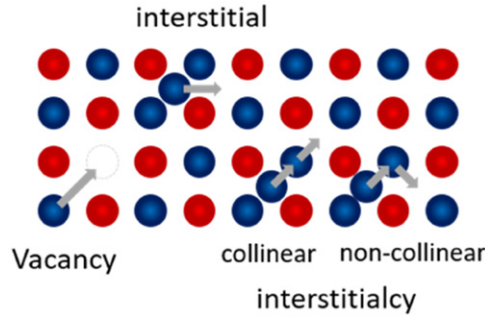


Fig. 6 Illustration of typical diffusion mechanisms: Vacancy (left), interstitial (center) and collinear as well as non-collinear interstitialcy (right).

$$[V_{\text{Ce}}^{\text{'''}}] = \frac{4K_S}{[V_{\text{O}}^{\bullet\bullet}]^2 a_{\text{CeO}_2}} = \frac{4K_S}{K_{\text{AF}}^2} \left(\frac{K_{\text{O}}}{4} \right)^{1/3} a_{\text{O}_2}^{1/6} \quad (2.53)$$

$$[\text{Ce}_i^{\bullet\bullet\bullet}] = \frac{K_F}{[V_{\text{Ce}}^{\text{'''}}]} = \frac{K_{\text{AF}}^2 K_F}{4K_S} \left(\frac{K_{\text{O}}}{4} \right)^{-1/3} a_{\text{O}_2}^{-1/6} \quad (2.54)$$

The Kröger-Vink diagram is obtained by combining the four partial pressure regions. The defect fractions depend on the oxygen activity in a double-logarithmic plot as in Fig. 5. Most notably are the individual slopes in each region that result from the exponents of the oxygen activity.

Of course it is possible to solve the set of equations numerically for the whole range of oxygen partial pressures. However, as demonstrated above, we are able to deduce the oxygen partial pressure dependence of the molar fractions with only a qualitative knowledge of the defect chemistry. This approach is especially helpful for characterizing defect chemistry in new materials where the values of the individual equilibrium constants are not known.

Mobility and Conductivity

Diffusion

According to Eq. (1.2), the ionic conductivity does not only depend on the concentration of the defects but also on their mobility. The mobility of the ions is directly related to their diffusivity, expressed by the diffusion coefficient D in the Nernst-Einstein relation

$$\mu = \frac{qD}{k_B T}. \quad (3.1)$$

The diffusion coefficient is found in Fick's first law which describes the diffusion flux j in a concentration gradient as shown for the x -direction in the one-dimensional case:

$$j = -D \frac{dc}{dx} \quad (3.2)$$

Due to the negative sign, the ions move down the gradient leading to its flattening. The temporal change of the concentration can be described by Fick's second law

$$\frac{dc}{dt} = \frac{d}{dx} \left(D \frac{dc}{dx} \right) \quad (3.3)$$

or, by assuming that the diffusion coefficient is constant throughout the volume,

$$\frac{dc}{dt} = D \frac{d^2 c}{dx^2}. \quad (3.4)$$

Phenomenologically, a temperature dependence of the diffusion coefficient is observed that can be expressed by the Arrhenius-type equation

$$D = D_0 \exp \left(-\frac{E_A}{k_B T} \right) \quad (3.5)$$

where D_0 represents the diffusion at infinite temperature. The phenomenological activation energy E_A results from the motion of ions on the microscopic level and depends on composition, structure and mechanism. Three typical migration mechanisms can be distinguished as depicted in Fig. 6: (1) The vacancy mechanism, in which a regular ion jumps to a neighboring vacant site. (2) The interstitial mechanism, in which an interstitial ion jumps to another empty interstitial site. (3) The interstitialcy mechanism, in which an interstitial displaces a regular ion from its position to another interstitial site and takes the regular position. This mechanism can proceed in a collinear or non-collinear fashion.

In a descriptive picture, the ions are vibrating around their equilibrium position trying to jump to a neighboring site by overcoming the migration barrier E_{mig} . With the attempt frequency ν_0 , the number of jumps n per time t is given by the jump rate

$$\Gamma = \frac{n}{t} = \nu_0 \cdot \exp\left(-\frac{E_{\text{mig}}}{k_B T}\right). \quad (3.6)$$

To link the microscopic movements of the defects to the macroscopic diffusion coefficient, we can follow the motion of a single vacancy. For the sake of simplicity, we restrict motion to one dimension where the vacancy randomly performs a jump of length $-d$ or $+d$ in every step. After n steps the total displacement Δx is the sum over all the steps. Averaging over m independent runs or m independent vacancies give the expected value of the displacement.

$$\langle \Delta x \rangle = \frac{1}{m} \sum \Delta x \quad (3.7)$$

As the individual jumps are uncorrelated, Δx becomes zero without any external driving force such as an electric field or a gradient in the chemical potential. In contrast, the mean squared displacement in x -direction is not zero and can be written as:

$$\langle (\Delta x)^2 \rangle = nd^2 \quad (3.8)$$

With the definition of the jump rate in Eq. (3.6) the diffusion coefficient for the vacancies is obtained as

$$D_V = \frac{d^2}{6} \Gamma_V, \quad (3.9)$$

where the factor 6 originates from the six directions in a 3-dimensional lattice.

Each jump of a vacancy is accompanied by an opposite jump of an ion and the diffusion coefficient D of the ions is directly related to the diffusion coefficient of the vacancies

$$D = \frac{c_V}{c_{\text{ion}}} D_V \approx n_V D_V \quad (3.10)$$

Here, n_V is the site fraction of vacancies and the approximation in Eq. (3.10) holds for $c_V \ll c_{\text{ion}}$, which is the case in most materials.

However, the diffusion coefficient of the ions is generally not measurable due to the correlated nature of the motion. Instead, the tracer diffusion coefficient D^* is measured which is connected to D by the tracer correlation factor f^* :

$$D^* = f^* \cdot D \quad (3.11)$$

Conductivity

With an applied electric field E , the flux density of ions j can be described according to Ohm's law

$$j = \frac{\sigma}{q} E. \quad (3.12)$$

On the microscopic level, the flux can be explained by a tilting of the energy landscape leading to higher and lower barriers in forward and backward direction depending on the ionic charge q , expressed by

$$\Delta E_{\text{mig}}^{\pm} = \Delta E_{\text{mig}} \mp \frac{qdE}{2}. \quad (3.13)$$

In the one-dimensional case, the average displacement in the electric field can then be expressed by

$$\langle x \rangle = t \frac{d}{2} \nu_0 \left[\exp\left(-\frac{\Delta E_{\text{mig}} - \frac{qdE}{2}}{k_B T}\right) - \exp\left(-\frac{\Delta E_{\text{mig}} + \frac{qdE}{2}}{k_B T}\right) \right]. \quad (3.14)$$

For sufficiently weak electric fields, i.e. $qdE/2 \ll k_B T$, the displacement is a linear response of the electric field expressed as

$$\langle x \rangle = t \frac{qd^2}{2k_B T} \nu_0 E \exp\left(-\frac{\Delta E_{\text{mig}}}{k_B T}\right). \quad (3.15)$$

The mobility can now be calculated from the drift velocity $v = \langle x \rangle / t$ by:

$$\mu = \frac{v}{E} = \frac{qd^2}{2k_B T} \nu_0 \exp\left(-\frac{\Delta E_{\text{mig}}}{k_B T}\right) = \frac{qd^2}{2k_B T} \Gamma \quad (3.16)$$

Considering Eq. (3.6) and turning from ΔE_{mig} to the more general activation energy E_A the temperature dependence of the ionic conductivity can be expressed by

$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{E_A}{k_B T}\right) \quad (3.17)$$

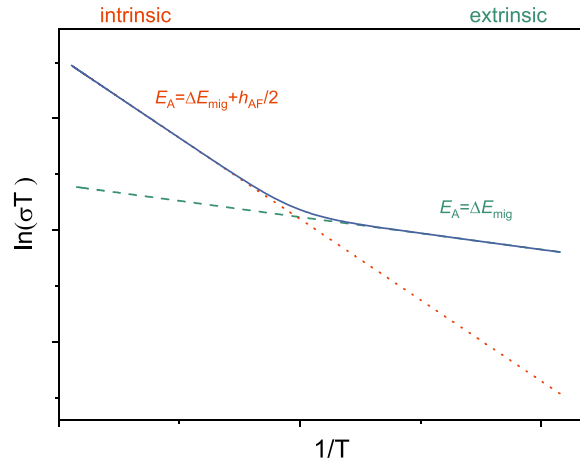


Fig. 7 Illustration of the change of activation energy between intrinsic and extrinsic regime.

or the linearized form

$$\ln(\sigma T) = \ln \sigma_0 - \frac{E_A}{k_B T}. \quad (3.18)$$

The phenomenological activation energy E_A is only seldomly equal to the microscopic migration barrier ΔE_{mig} . Instead, the activation energy might be written as

$$E_A = \Delta E_{\text{mig}} + \Delta E_{\text{ass,eff}} + \Delta E_{\text{form,eff}} \quad (3.19)$$

where, the term $\Delta E_{\text{form,eff}}$ and $\Delta E_{\text{ass,eff}}$ refer to effective energy contributions due to the formation of defects and defect associations, respectively.

Contribution of the Defect Formation

With Eqs. (1.2) and (3.16), we can express the ionic conductivity by

$$\sigma = c \frac{q^2 d^2}{2k_B T} v_0 \exp\left(-\frac{\Delta E_{\text{mig}}}{k_B T}\right) = \frac{c \mu_0}{T} \exp\left(-\frac{\Delta E_{\text{mig}}}{k_B T}\right). \quad (3.20)$$

Let us assume an AO crystal with dominating anti-Frenkel disorder, where the oxygen vacancies are mobile. With the expression for the fraction of anti-Frenkel defects, we can rewrite Eq. (3.20) as

$$\sigma = \frac{c_0 \mu_0}{T} \exp\left(-\frac{\Delta E_{\text{mig}}}{k_B T}\right) \exp\left(-\frac{\Delta g_{\text{AF}}}{2k_B T}\right) = \frac{c'_0 \mu_0}{T} \exp\left(-\frac{2\Delta E_{\text{mig}} + \Delta h_{\text{AF}}}{2k_B T}\right) \quad (3.21)$$

where the constant c'_0 contains the temperature independent quantities related to the defect concentration. The effective activation energy now includes an additional contribution $\Delta h_{\text{AF}}/2$. We consider doping with B'_A with the charge neutrality condition

$$2[V_O^{\bullet\bullet}] = 2[O_i''] + [B'_A]. \quad (3.22)$$

Combining with the mass action law for anti-Frenkel disorder we obtain

$$2[V_O^{\bullet\bullet}] = 2 \frac{K_{\text{AF}}}{[V_O^{\bullet\bullet}]} + [B'_A]. \quad (3.23)$$

The solution of this quadratic equation yields the fraction of oxygen vacancies depending on dopant fraction and equilibrium constant:

$$[V_O^{\bullet\bullet}] = \frac{[B'_A]}{4} + \sqrt{\left(\frac{[B'_A]}{4}\right)^2 + K_{\text{AF}}} \quad (3.24)$$

For low temperatures with $K_{\text{AF}} \ll \left(\frac{[B'_A]}{4}\right)^2$ we find $2[V_O^{\bullet\bullet}] = [B'_A]$. Thus, the conductivity is determined by extrinsic defects and $E_A = \Delta E_{\text{mig}}$. For high temperatures where $K_{\text{AF}} \gg \left(\frac{[B'_A]}{4}\right)^2$, the conductivity is determined by intrinsic defects $[V_O^{\bullet\bullet}] = \sqrt{K_{\text{AF}}}$ and we obtain $E_A = \Delta E_{\text{mig}} + \Delta h_{\text{AF}}/2$. In the intermediate regime, E_A is a function of the temperature itself as illustrated in Fig. 7.

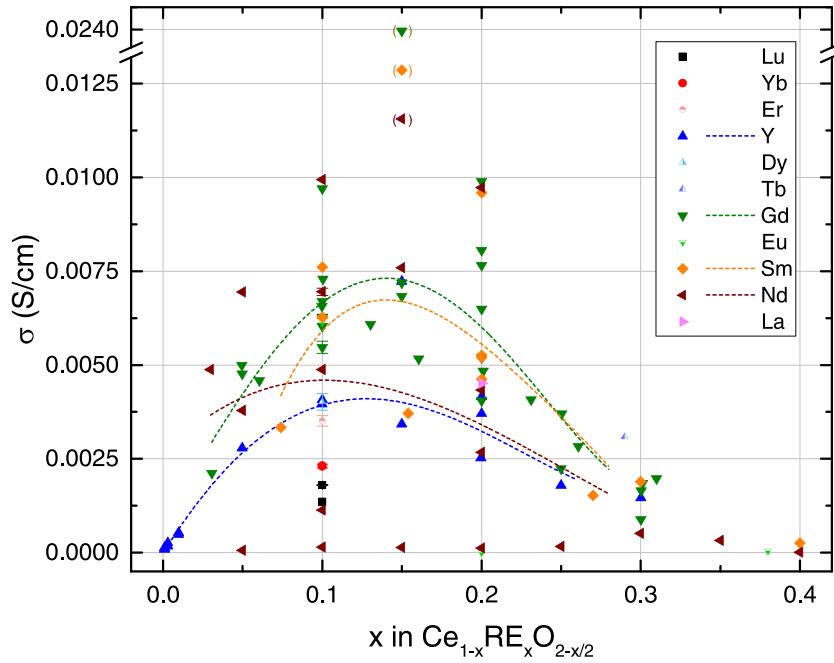


Fig. 8 Compilation of measured ionic conductivities in doped ceria at 500°C for different dopants. Reproduced from Koettgen, J., Grieshammer, S., Hein, P., *et al.*, 2018. Understanding the ionic conductivity maximum in doped ceria: Trapping and blocking. *Physical Chemistry Chemical Physics* 20, 14291–14321 with permission from the Royal Society of Chemistry.

Contribution of Defect Association

The contribution of defect association to the activation energy is described by the $\Delta E_{\text{ass,eff}}$ term in Eq. (3.19). In a simple approach, defect associates such as pairs and triplets can be defined. A typical example is an immobile dopant $D^\bullet$ associated with a mobile vacancy V' . The formation of the defect pair $(D^\bullet - V')^\times$ can be expressed by the reaction



with the corresponding mass action law

$$K_{\text{ass}} = \frac{[(D^\bullet - V')^\times]}{[D^\bullet][V']} = e^{-\frac{\Delta G_{\text{ass}}}{k_B T}}. \quad (3.26)$$

From the charge neutrality condition $[D^\bullet] = [V']$ and the total dopant fraction $x = [(D^\bullet - V')^\times] + [D^\bullet]$ we can rewrite this equation as

$$K_{\text{ass}} = \frac{x - [V']}{[V']^2}. \quad (3.27)$$

Solving for $[V']$ results in the molar fraction of 'free', unassociated vacancies.

$$[V'] = -\frac{1}{2K_{\text{ass}}} + \left(\frac{1}{4K_{\text{ass}}^2} + \frac{x}{K_{\text{ass}}} \right)^{1/2} = -\frac{1}{2K_{\text{ass}}} + \frac{1}{2K_{\text{ass}}} (1 + 4xK_{\text{ass}})^{1/2} \quad (3.28)$$

In the limit of weak association with small values of xK_{ass} we obtain $[V'] \approx x$. In the limit of strong association with large values of xK_{ass} we obtain $[V'] \approx \left(\frac{x}{K_{\text{ass}}} \right)^{1/2}$. In a simple picture, only the free vacancies are regarded as mobile and contribute to the ionic conductivity.

We note that this is a rough estimate as the vacancies are not permanently trapped by the dopant but there is a dynamic equilibrium between free and trapped vacancies. Furthermore, the approach is only reasonable for rather dilute defects, whereas for higher defect concentrations more extended defect clusters emerge and the definition of definite associates could become difficult.

Typical examples for this behavior are found in fluorite structures such as yttria stabilized zirconia and doped ceria. Fig. 8 shows a compilation of measured bulk conductivities of ceria doped with various rare-earth elements. A maximum in the conductivity can be observed at rather low dopant fraction. On the one hand, the number of oxygen vacancies increases with the dopant fraction according to Eq. (2.29). On the other hand, the activation energy increases due to the interactions between the vacancies and the dopant ions. These interactions include the trapping of oxygen vacancies by the immobile dopants due to attractive interactions and the blocking of the migration path due to the larger size of the dopant ions (Grieshammer *et al.*, 2014; Koettgen *et al.*, 2018).

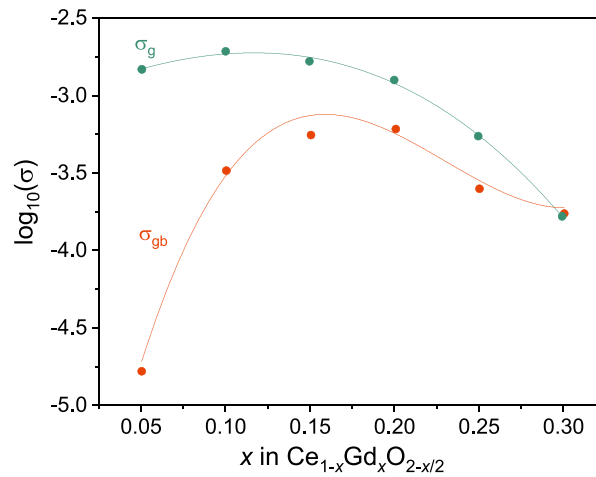


Fig. 9 Ionic conductivity of the interior of the grain (green) and grain boundaries (red) in doped ceria at 400°C. Data from Tianshu, Z., Hing, P., Huang, H., Kilner, J., 2002. Ionic conductivity in the CeO₂-Gd₂O₃ system (0.05 ≤ Gd/Ce ≤ 0.4) prepared by oxalate coprecipitation. Solid State Ionics 148, 567–573. Lines are guide to the eye only.

As shown in Fig. 8, ceria provides high ionic conductivity. The high substitution level of several percent ensures that the defect chemistry is dominated by the charge neutrality condition $[Y'_{Ce}] = 2[V_O^{\bullet\bullet}]$ over a broad range of oxygen partial pressures. Nevertheless, the mobility of the electrons is orders of magnitude higher than the mobility of the vacancies. Thus, even minority electrons can significantly contribute to the overall conductivity under reducing conditions.

This is problematic for the application as an electrolyte, e.g., in a solid oxide fuel cell. Electronic conductivity in the electrolyte leads to leakage current, thus reducing the efficiency of the cell. Accordingly low oxygen partial pressures are obtained at the negative electrode side of a solid oxide fuel cell. The proportion of the partial conductivities is expressed by the transference number.

$$t_i = \frac{\sigma_i}{\sigma_{\text{total}}} \quad (3.29)$$

As the cations are slow in ceria, the total conductivity σ_{total} is composed of the oxygen ion and the electronic conductivity. For an efficient electrolyte, $t_{\text{ion}} \approx 1$ is mandatory and the corresponding region in the corresponding Kröger-Vink diagram is called the 'ionic domain'.

Effect of Grain Boundaries

So far, we considered the ionic conductivity due to point defects in the bulk materials without any extended defects. In contrast, real materials are rarely single crystals but polycrystalline, i.e., multiple grains are separated by grain boundaries. Moving ions have to cross the grain boundaries to transfer from one grain to another. In addition, movement along the grain boundaries can be far different from the value in the grain. Indeed, the mobility of the ions across or along the grain boundary can be far different from the value in the grain.

Both cases, acceleration of ions in the grain boundary as well as mitigation of the ionic mobility have been observed. Nevertheless, blocking grain boundaries seem to be the general case for ionic conduction in oxides. As an example, Fig. 9 shows the grain boundary and bulk conductivity in doped ceria as measured by impedance spectroscopy.

An extensive explanation for the lower mobility in the grain boundaries is not yet available. Possible reasons are:

- The distorted structure of the grain boundary leading to an increase of the migration barrier.
- Impurity segregation and formation of secondary phases at the grain boundary with low conductivity.
- The formation of a space charge zone at the grain boundary leading to a depletion of the charge carrier concentration.

Summary

Ionic conductivity in oxide materials is important in a wide field of technological applications including efficient energy storage. The magnitude of the conductivity depends on the concentration of defects in the crystal lattice and their mobility. In this article, the principles of defect formation and calculation of defect concentrations as well as the migration mechanisms of defects were discussed.

Defects can be created by intrinsic disorder of the lattice, oxidation and reduction or by the substitution with secondary materials. In general, all of these formation processes are present, although the defect chemistry is mostly governed by one pair of majority defects.

Transport of ions in the lattice is possible by vacancy, interstitial, and interstitialcy migration with the mobility depending on the associated migration barrier that reflects the energy required to transfer an ion between two distinct positions. In contrast, the

phenomenological activation energy of ionic conductivity can include contributions from the formation and interaction of defects. In addition, the total conductivity in a polycrystalline material is affected by both the conductivity in the interior of the grains and at the grain boundaries, which can diverge by orders of magnitude.

The search for complex oxides with high ionic conductivity is an active field in chemistry and material science and optimization of materials is crucial for technological applications. Therefore, knowledge of the principles of ionic conductivity in oxides is crucial for both experimental and computational approaches.

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High Entropy Oxides

Abhishek Sarkar, KIT-TUD Joint Research Laboratory Nanomaterials – Technical University of Darmstadt, Darmstadt, Germany and Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

Horst Hahn, KIT-TUD Joint Research Laboratory Nanomaterials – Technical University of Darmstadt, Darmstadt, Germany; Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany; and School of Chemical, Biological and Materials Engineering, The University of Oklahoma, Norman, OK, United States

Robert Kruk, Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

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Abstract

High entropy oxides (HEOs) are an emerging class of single-phase oxide solid solutions consisting of multiple cations in near-equiatomic proportions occupying a given cation sub-lattice. The vast composition space of HEOs offers a wide range of possibilities for tailoring properties, many of which are the result of their diverse cationic environment. This article provides an overview of the current state of research on HEOs, encompassing their classification based on configurational entropy, synthesis routes, important classes and compositions, phase stability mechanisms, and properties. Finally, the latest developments in high-throughput experimental techniques for accelerated composition screening of HEOs, which are inherently crucial for future HEO research, are presented.

Key Points

- Definition and configurational entropy based classification of high entropy oxides (HEOs).
- Different classes of HEOs and related synthesis routes.
- Factors underpinning the phase purity and related phase transformations in HEOs.
- Different functional properties of HEOs and underlying mechanisms.

Introduction

The development of new materials is a prerequisite for meeting today's technological demands. There are multiple approaches to materials design, among which changing the composition of a given system, usually referred to as alloying for metallic and doping for non-metallic ones, is undoubtedly the most common approach. Alloying or doping conventionally means the introduction of relatively small amounts of secondary elements into a "base" system, which (typically) consists of one major component, e.g., Fe is the base system for steels, while ZrO_2 is the base for yttria-stabilized zirconia. In contrast, Cantor (Cantor *et al.*, 2004) and Yeh (Yeh *et al.*, 2004) independently pioneered an unorthodox approach to alloy design by adding multiple elements (typically ≥ 5) and, importantly, all in (nearly) equiatomic proportions. Hence, there is no base component ("baseless") as such in these alloys. Interestingly, many of these alloys, despite being compositionally complex (owing to the presence of multiple-principal elements), crystallize as phase-pure solid solutions or exhibit a much smaller number of phases compared to the maximum allowed by the Gibbs phase rule (Cantor *et al.*, 2004; Murty *et al.*, 2014; Yeh *et al.*, 2004). Accordingly, Yeh *et al.* (2004) proposed that the tendency to form a single-phase solid solution may be related to the increased (configurational) entropy of mixing (ΔS_{mix}), resulting from the presence of a large number of constituents in near-equiatomic proportions, and consequently coined the term "high entropy alloys (HEAs)". Another advantage offered by this unconventional design approach, i.e., the introduction of multiple elements in near-equiatomic proportions, is the possibility to investigate the "unexplored central regions" of multinary phase diagrams where potentially unique properties can stem from synergistic effects. Given these alternative motivations, namely the use of configurational entropy to control phase composition and the ability to tailor properties by exploiting synergies in previously unknown central regions of multicomponent phase diagrams, the HE based design approach has now been extended to other types of materials beyond metallic HEAs.

Research interest in high entropy non-metallic materials (HEMs) is largely fueled by the discovery of high entropy oxides (HEOs) (Rost *et al.*, 2015). Despite being at its early stage, the HEO-research field has grown rapidly to include several classes of oxides with different crystallographic structures and compositions (Musicó *et al.*, 2020; Oses *et al.*, 2020; Sarkar *et al.*, 2019, 2020a). Importantly, the compositional flexibility of HEOs, i.e., ability to maintain phase purity despite compositional complexity, provides greater opportunities to tune their properties. In this context, various studies already highlight the unique, and often enhanced, functionalities exhibited by HEOs (Akrami *et al.*, 2021; Musicó *et al.*, 2020; Sarkar *et al.*, 2019, 2020a). The focus of this article is on this emerging class of multifunctional, compositionally complex HEOs. We begin with Section "Introduction", by discussing the definition of HEOs and entropy-based oxides classification. In Section "Definition and Classification", the different HEOs classes and synthesis routes are presented. In Section "Different Classes of HEOs and Synthesis Routes", the underlying factors governing the stability of single-phase HEOs are discussed. Selected properties that appear to be unique to

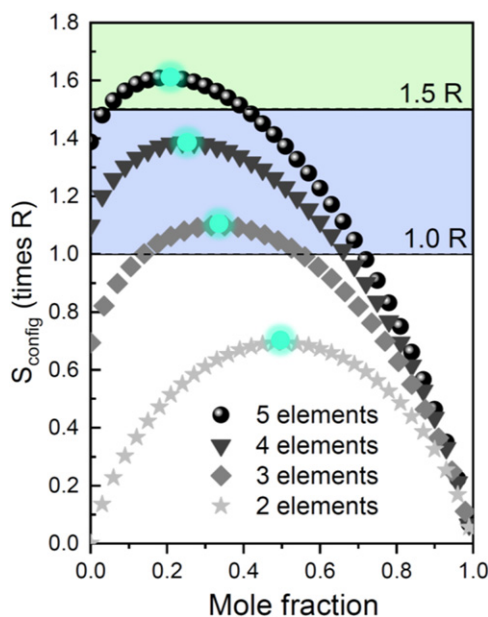


Fig. 1 Dependence of configurational entropy (S_{config}) on the number of elements and their respective mole fractions. The green (highlighted) circles indicate the equiatomic compositions for the respective systems, which result in their highest S_{config} . Systems with $S_{\text{config}} \geq 1.5 R$ are classified as “high entropy”, the ones with $1 R \leq S_{\text{config}} < 1.5 R$ are regarded as “medium entropy” and the systems with $S_{\text{config}} < 1 R$ fall under the category of the low entropy. Reproduced from Sarkar, A., Wang, Q., Schiele, A., *et al.*, 2019. High-entropy oxides: Fundamental aspects and electrochemical properties. *Adv. Mater.* 31, 1806236. Available at: <https://doi.org/10.1002/adma.201806236>. Adapted under the terms of the CC BY-NC-ND 4.0 license, copyright 2019, the authors, published by Wiley.

HEOs or strongly influenced by the HE-design approach are discussed in Section “Phase Stability Mechanisms”. Finally, in Section “Properties and Underlying Principles”, the latest developments in high-throughput-based experimental techniques and theoretical studies that are important for the rational design of HEOs are presented.

Definition and Classification

As mentioned earlier, the term “high entropy” was first coined by Yeh and co-workers for describing the multicomponent equiatomic HEAs (Murty *et al.*, 2014; Yeh *et al.*, 2004). Their hypothesis was based on two well-known equations (Eqs. 1 and 2) relevant for the formation of solid-solutions:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (1)$$

$$\Delta S_{\text{mix}} = -R \text{Bigg} \left[x \text{Bigg} \left(\sum_{i=1}^N x_i \ln x_i \text{Bigg} \right) \text{Bigg} \right] \quad (2)$$

In Eqs. 1 and 2, the terms ΔG_{mix} , ΔH_{mix} , ΔS_{mix} , T , R , N and x_i stand for free energy of mixing, enthalpy of mixing, entropy of mixing (considered identical to configurational entropy, S_{config}), temperature, universal gas constant, number of elements and the corresponding mole fractions, respectively. Eq. 2 indicates that the ΔS_{mix} (or S_{config}) increases with the presence of more elements and reaches its maxima for a given composition when all the elements are present in equiatomic proportion, as shown in Fig. 1. Correspondingly, Yeh *et al.* proposed that the presence of multiple elements (five or more) in near-equiatomic proportions, as is the case in HEAs, would increase the S_{config} to such an extent that $T\Delta S_{\text{mix}}$ would be able to readily overcome the ΔH_{mix} -penalty, thereby promoting the formation of single-phase solid solution over ΔH_{mix} supported phase separation. Based on this hypothesis, alloy systems with $S_{\text{config}} \geq 1.5 R$ are classified as HEAs. However, it is important to mention that $S_{\text{config}} \geq 1.5 R$ for a given composition does not necessarily guarantee the formation of a single phase solid solution as expected from the entropy-based hypothesis. Nevertheless, the entropy-based classification is still widely followed by researchers working on HEAs and other HEMs. Based on this entropy-based nomenclature, alloy systems can be further classified as medium entropy ($1 R \leq S_{\text{config}} < 1.5 R$) or low entropy ($S_{\text{config}} < 1 R$) (Murty *et al.*, 2014).

A similar entropy-based classification is adapted to oxides as well, where systems with $S_{\text{config}} \geq 1.5 R$ are classified as HEOs and systems with $1 R \leq S_{\text{config}} < 1.5 R$ as medium entropy oxides (MEOs). Nevertheless, there exists several confusions with the entropy-based classification for oxides. For instance, in the case of $\text{La}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$, which is a perovskite-type HEO (ABO_3), there are three different sub-lattices: two for the cations (A and B) and one for the anion (O). Hence, the S_{config} in such a system can be defined either in terms of $S_{\text{config}/\text{atom}}$, $S_{\text{config}/\text{f.u.}}$ (f.u. is formula unit) and $S_{\text{config}/\text{cations}}$. The S_{config} per mole of

atom ($S_{\text{config}}/\text{atom}$) with multiple sub-lattices can be calculated as follows:

$$\frac{S_{\text{config}}}{\text{atom}} = -R \left[\frac{z \sum_{z=1}^z a^z \sum_{y=1}^y (f_i^z \ln f_i^z)}{\sum_{z=1}^z a^z} \right] \quad (3)$$

where, a^z is the number of sites on the z sub-lattice, f_i^z is the fraction of elemental species randomly distributed on the respective sub-lattice and y is the number of elements in a given sub-lattice. For a 1:1:3 (ABO_3) perovskite oxide $\text{La}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$, Eq. 3 can be re-written as follows:

$$\frac{S_{\text{config}}}{\text{atom}} = -R \left[\frac{1 * \ln 1 + 1 * (0.2 \ln 0.2 * 5) + 3 * \ln 1}{5} \right] \quad (4)$$

Likewise, the $S_{\text{config}}/f.u.$ and $S_{\text{config}}/\text{cations}$ in ABO_3 perovskite can be defined as follows:

$$\frac{S_{\text{config}}}{f.u.} = 5 * \frac{S_{\text{config}}}{\text{atom}} \quad (5)$$

$$\frac{S_{\text{config}}}{\text{cation}} = \frac{5}{2} * \frac{S_{\text{config}}}{\text{atom}} \quad (6)$$

Although it remains unclear which S_{config} variant should be used for classification of HEO, the $S_{\text{config}}/f.u.$ is one that is most commonly found for classifying an oxide as HEO ($S_{\text{config}}/f.u. \geq 1.5 R$). Thus, HEOs can be defined as oxide solid solutions consisting of multiple cations (5 or more) in near-equimolar concentrations on a given cation sub-lattice.

Apart from this “ S_{config} -based” definition, there are several other terms that are often used to categorize HEOs, such as “entropy stabilized oxides” (Rost *et al.*, 2015), “multicomponent equiatomic oxides” (Djenadic *et al.*, 2017) and “compositionally complex oxides (ceramics)” (Wright and Luo, 2020). Detailed discussion regarding use of these different nomenclatures, alongside the mostly commonly used one, i.e., HEOs, can be found in several review reports (Brahlek *et al.*, 2022; Sarkar *et al.*, 2020a).

Next, we provide an overview of different classes of HEOs and the variety of synthesis routes used for obtaining them.

Different Classes of HEOs and Synthesis Routes

HEOs are largely categorized based on their crystal structure: rocksalt (Rost *et al.*, 2015), fluorite (Djenadic *et al.*, 2017), bixbyite (Sarkar *et al.*, 2017b), perovskite (Jiang *et al.*, 2018; Sarkar *et al.*, 2018a), spinel (Dąbrowa *et al.*, 2018; Fracchia *et al.*, 2020b; Musicó *et al.*, 2019), pyrochlore (Teng *et al.*, 2020), rutile (Kimbauer *et al.*, 2019), delafossite-type layered (Wang *et al.*, 2020; Zhao *et al.*, 2020) and magnetoplumbite (Vinnik *et al.*, 2019). Detailed information about the variety of compositions for each of these HEO classes can be found in some of the recent review articles (Akrami *et al.*, 2021; Musicó *et al.*, 2020). The initial reports on HEOs show promises that the HE-based design approach can be practically extended to all oxide crystal structures, motivating future research along this direction.

Different synthesis routes that are known for conventional oxides have been extended for the synthesis of HEO. Examples of the varied synthesis and processing routes known for HEOs are listed in Table 1. Likewise, depending upon the synthesis and processing routes different morphologies and microstructures of HEOs can be obtained. For instance, conventional solid state routes allow the synthesis of microcrystalline HEOs, while techniques like spray pyrolysis (Sarkar *et al.*, 2017a), sonochemistry (Okejiri *et al.*, 2020), mechanochemistry (Chen *et al.*, 2019), etc., result in nanocrystalline HEOs. In the later cases, either the residence time of the precursor/product at high temperature is short or the synthesis temperature itself is low prohibiting grain growth. A wide variety of techniques are also known for obtaining bulk HEO pellets with different microstructural features, such as conventional sintering, spark plasma sintering, flash sintering, etc., (Dupuy *et al.*, 2019; Kumar *et al.*, 2020). Epitaxial thin film deposition has also been reported for different types of HEOs (Kotsonis *et al.*, 2018; Sharma *et al.*, 2018). The possibility to tailor the structural features utilizing substrate induced epitaxial strain effects has further broadened the spectrum of property tailoring possibilities in HEOs.

Phase Stability Mechanisms

Initial studies indicate that the phase stability mechanisms differ among the various HEO classes, e.g., a few show entropy-driven phase stabilization, while in others, the presence of certain cations and the ionic radii are of greater importance. Although it is not straightforward to assign one single mechanism for phase stability of a given HEO as several factors coexist, we separate the three aforementioned contributions using different case studies to provide a simpler overview.

Table 1 Different synthesis and processing routes of HEOs

Product type	Techniques used	References
Powder	Conventional solid-state	Rost <i>et al.</i> (2015)
	Mechanochemical	Chen <i>et al.</i> (2019)
	Spray pyrolysis	Sarkar <i>et al.</i> (2017a)
	Hydrothermal	Biesuz <i>et al.</i> (2018)
	Co-precipitation	Sarkar <i>et al.</i> (2017a)
	Sonochemical	Okejiri <i>et al.</i> (2020)
	Solution combustion	Mao <i>et al.</i> (2019)
	Solvothermal	Wang <i>et al.</i> (2019)
	Polymeric steric entrapment	Tseng <i>et al.</i> (2020)
	Conventional sintering	Bérardan <i>et al.</i> (2016b)
Pellet	Spark plasma sintering	Dupuy <i>et al.</i> (2019)
	Flash sintering	Kumar <i>et al.</i> (2020)
Thin films	Pulsed laser deposition	Sharma <i>et al.</i> (2018)
	Magnetron sputtering	Kirnbauer <i>et al.</i> (2019)

Note: Reproduced from Sarkar, A., Breitung, B., Hahn, H., 2020a. High entropy oxides: The role of entropy, enthalpy and synergy. *Scr. Mater.* 187, 43–48. Available at: <https://doi.org/10.1016/j.scriptamat.2020.05.019>.

Entropy-Driven Phase Stabilization

As discussed earlier, one of the primary hypotheses is that in the case of HEMs the ΔS_{mix} (or S_{config}) is large enough to stabilize single-phase solid solution over a wide range of temperature (T) overcoming ΔH_{mix} -penalties, as per Eq. 1. Although this entropy-based hypothesis lacks generality, some HEO systems, for instance the transition metal (TM) based rocksalt-HEOs, ($\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$), do show strong degree of entropy-driven phase stabilization. In ($\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$) a reversible phase transformation is observed where a single-phase solid solution that is obtained at high temperature dissociates to multiple phases at lower temperature (Rost *et al.*, 2015). Cyclic heat treatment at high and low temperatures further highlights the reversibility of the phase transformation, as shown in Fig. 2a. This observation can be explained via an entropy-driven phase stabilization mechanism. At high temperatures, the entropy dominated single phase solid solution is preferred, whereas enthalpy driven phase segregation occurs at lower temperatures as the ΔG_{mix} to form a single phase becomes positive. The association of an endothermic reaction (Fig. 2b) during transformation of the multiphase mixture to single phase solid solution, further strengthens the claim of entropy-driven single phase stabilization (Biesuz *et al.*, 2018; Rost *et al.*, 2015). Additionally, the requirement of a higher temperature (independent of the composition) to form a single-phase MEO (with lower S_{config}) solid solution with 4 constituent cations, such as ($\text{Co}_{0.25}\text{Mg}_{0.25}\text{Ni}_{0.25}\text{Zn}_{0.25}\text{O}$), compared to five cation ($\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$)-HEO, further highlights the claim of entropy-driven single phase stabilization (Rost *et al.*, 2015; Sarkar *et al.*, 2018b, 2020a). Molecular dynamic (MD) simulations, additionally, support this observation (Anand *et al.*, 2018). Consequently, the HEO systems, which show such dominant role of entropy (especially highlighted by the reversible phase transition) are often categorized as “entropy-stabilized oxides”. Currently, only a handful of HEO systems (Chen *et al.*, 2018; Dragoe and Bérardan, 2019; Rost *et al.*, 2015; Sarkar *et al.*, 2018a; Spiridigliozzi *et al.*, 2020) exhibit the phenomena of entropy stabilization. It should also be noted that the reversible transformation from multiple phases to single phase upon cyclic heat treatment considered, which is considered as the signature of entropy-driven phase stabilization, is not only limited to HEOs but has also been observed in low entropy systems such as $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{O}$ and $\text{Ni}_{0.6}\text{Zn}_{0.2}\text{Cu}_{0.2}\text{O}$ (Frachia *et al.*, 2022).

Role of Cationic Radii and Oxidation State in Phase Stability

Similar to conventional oxides, cationic radii and oxidation state of the cations still play crucial roles in determining the phase stability of HEOs. Likewise, well-known ionic radii and oxidation state-based criteria following Pauling rules (for structure and local coordination of cation), Hume-Rothery rules (for solution formation) and Goldschmidt’s tolerance factor (for structure) can still be used to elucidate the HEO phases that are formed. Consequently, a parameter based on the difference of the cationic size (δ_r) on a given cation sub-lattice (Eq. 7) is often used as yardstick to predict phase-stability of HEMs/HEOs (Jiang *et al.*, 2018).

$$\delta_r = \sqrt{\sum_{i=1}^N c_i \text{Bigg} (1 - r_i / \text{Bigg} (\sum_{i=1}^N c_i r_i \text{Bigg}) \text{Bigg})^2} \quad (7)$$

In Eq. 7, N is the number of cations, r_i is the radius of the i^{th} cation at the given cation sub-lattice and c_i is the mole fraction of the i^{th} cation. It is considered that a single phase is formed if the $\delta_r < \sim 6.5\%$. Another ionic radii based parameter, termed as mean radii ($M.R.$), is also used to determine stability of certain crystallographic structures (such as fluorite over bixbyite or

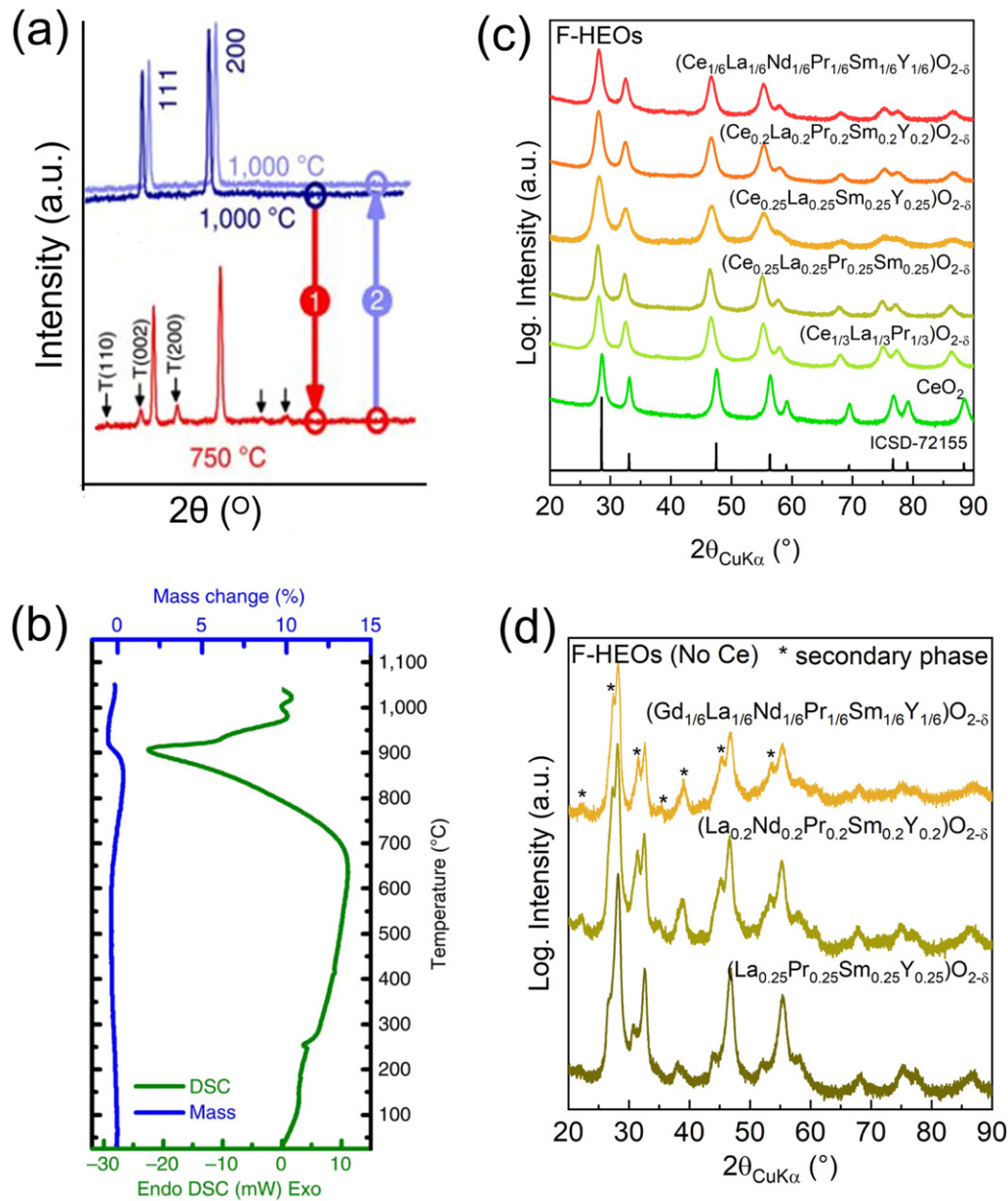


Fig. 2 Two different types of phase stability mechanisms in HEOs are illustrated here, (a) and (b) depict the scenario for entropy-driven phase stabilization in rocksalt-HEOs, while (c) and (d) highlight the crucial role of a single cation in the phase stability of fluorite-HEOs. Reproduced under the terms of the CC-BY 4.0 license Rost, C.M., Sachet, E., Borman, T., *et al.*, 2015. Entropy-stabilized oxides. Nat. Commun. 6, 8485. Available at: <https://doi.org/10.1038/ncomms9485>. Copyright 2015, the authors, published by Springer Nature. Djenadic, R., Sarkar, A., Clemens, O., *et al.*, 2017. Multicomponent equiatomic rare earth oxides. Mater. Res. Lett. 5, 102–109. Available at: <https://doi.org/10.1080/21663831.2016.1220433>. Copyright 2017, the authors, published by Taylor and Francis

pyrochlore) in HEOs, as dictated by Eq. 8 (Spiridigliozzi *et al.*, 2021), where M is the number of cations, r_j is the radii of the individual cations on the given sub-lattice and $\bar{r}$ is the average/mean radii.

$$M.R. = \sqrt{\frac{\sum_{j=1}^M (r_j - \bar{r})^2}{N - 1}} \quad (8)$$

It has been observed that rare-earth based systems with $M.R. > 0.095$ result in single-phase fluorite structure, while systems with $M.R. < 0.095$ show preferences of forming dual-phases (fluorite + bixbyite) mixtures at low temperatures and a single-phase bixbyite at higher temperatures (Spiridigliozzi *et al.*, 2021).

Although these ionic radii and oxidation state based yardsticks (Pauling rules, Hume-Rothery rules, Goldschmidt's tolerance factor, δ_r and $M.R.$) are helpful in explaining and predicting several HEO cases, multiple exceptions (Jiang *et al.*, 2018; Sarkar *et al.*, 2018a, 2022b) limit the use of these parameters to draw general conclusions regarding phase-stability or structure of HEOs.

Role of Individual Cations in Phase Stability

A unique phase stability mechanism is observed in the case of some fluorite-HEOs. For instance, equiatomic combinations of Ce, La, Pr, Sm and Y crystallize in single phase fluorite structure $(\text{Ce}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_{2-\delta}$ with the only pre-requisite being the presence of Ce (Djenadic *et al.*, 2017), Fig. 2c. Likewise, $(\text{Zr}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_{2-\delta}$ crystallizes in a single phase fluorite structure with the prerequisite being the presence of Zr (Sarkar *et al.*, 2022b). In fact, to the best of our knowledge, single phase fluorite-HEOs either have Ce and/or Zr as one of their constituents (Chen *et al.*, 2018; Djenadic *et al.*, 2017; Gild *et al.*, 2018; Musicó *et al.*, 2020; Sarkar *et al.*, 2020a, 2022b). Likewise, independent of the number of incorporated elements (i.e., the resulting S_{config}) or synthesis parameters, rare-earth (RE) based systems without Ce or Zr always exhibit multiple phases (as shown in Fig. 2d). Primarily, this indicates that the formation of a single-phase fluorite only with cations like (Gd, Nd, La, Pr, Sm, Tb, Eu, Sn, and Y) is not thermodynamically favorable. However, single phase can be achieved even with a small amount of Ce (Fig. 2a) or Zr, i.e., around 20% of the overall cations in the case of a five cation system like $(\text{Ce}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_{2-\delta}$ or $(\text{Zr}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_{2-\delta}$. One explanation of this behavior can be the stable $4+$ oxidation state of Ce/Zr, which is important for fluorite oxides. However, oxidation state might not be the only criteria as Ce/Zr replaced by Sn^{4+} , or a mixture of $\text{Pr}^{3+/4+}$ and $\text{Tb}^{3+/4+}$ resulting equivalent amount of $4+$, does not result in phase-pure HEOs (Sarkar *et al.*, 2022b). This certainly indicates that these cations (Ce/Zr) play a special role in stabilizing fluorite-HEOs, which simply cannot be explained using oxidation state, ionic radii or the S_{config} based criteria.

Overall, these diverse phase stability mechanisms make the HEOs unique from the fundamental perspective, motivating further research to better understand the reason of phase stability in HEOs. This is crucial for their rational design and composition optimization to achieve targeted properties.

Properties and Underlying Principles

A wide variety of properties has been reported for HEOs, spanning from dielectric (Bérardan *et al.*, 2016a, 2017), ionic transport (Bérardan *et al.*, 2016b), optical (Sarkar *et al.*, 2017a, 2020b, 2022b), magnetic (Meisenheimer *et al.*, 2017; Sarkar *et al.*, 2022c; Witte *et al.*, 2019, 2020; Zhang *et al.*, 2019), catalytic (Chen *et al.*, 2019; Chen *et al.*, 2018; Wang *et al.*, 2019), mechanical (Hong *et al.*, 2019), thermal (Braun *et al.*, 2018; Gild *et al.*, 2018) to electrochemical energy storage (Qiu *et al.*, 2019; Sarkar *et al.*, 2019). Exhaustive lists of these properties, along with the compositions and crystal structures of the respective HEOs, are well-documented in several review articles (Akrami *et al.*, 2021; Ma *et al.*, 2021; Musicó *et al.*, 2020; Oses *et al.*, 2020). In this section, as examples, we will focus on three specific properties of HEOs, electrochemical, thermal transport and magnetic, which have been the focus of the majority of current HEO research.

Electrochemical Properties

Two of the avenues where HEOs have shown remarkable performance compared to isostructural conventional oxides counterparts are electrochemical energy storage and catalysis. Numerous research works have demonstrated that HEOs can be used as electrodes, both as anode and cathode materials, in rechargeable Li-ion (Qiu *et al.*, 2019; Sarkar *et al.*, 2018b, 2019) and Na-ion batteries (Zhao *et al.*, 2020), Fig. 3a. HEOs often exhibit enhanced capacity along with better cyclic stability compared to the conventional oxides. In many cases, it is hypothesized that the enhanced structural stability of HEOs, plausibly stemming from the entropy-driven phase stabilization, benefits their cyclic performance (Moździerz *et al.*, 2022; Sarkar *et al.*, 2018b; Q. Wang *et al.*, 2019). Another research direction involves the optimization of the redox potential of batteries using the HE-design approach. The redox potential in batteries is largely governed by the inductive effect, which is related to the nature of the M-O-X bonds (where M is the metal cation, O is oxygen and X is another anion). The HE-design approach offers the flexibility to vastly change the cation or even the anion (from O^{2-} to F/Cl) while retaining the phase purity (Lun *et al.*, 2021; Moździerz *et al.*, 2022; Sarkar *et al.*, 2018b; Wang *et al.*, 2019). Subsequently, fine tuning of the redox potentials is possible, allowing the use of HEO or HEO based hetero-anionic systems as both anodes and cathodes in rechargeable Li-ion or Na-ion batteries (Lun *et al.*, 2021; Sarkar *et al.*, 2018b; Wang *et al.*, 2019; Zhao *et al.*, 2020).

The relation between enhanced catalytic activity and the chemical disorder offered by the HE-design approach has been observed in a wide variety of HEMs, such as HEAs, HEOs, HE-fluoride, etc., (Li *et al.*, 2021; Ma *et al.*, 2021; Sun and Dai, 2021). The catalysis directed research on HEMs, especially on the HEAs, has been motivated by the fact that these systems have varying surface metal sites with highly tunable adsorption energies for the reaction intermediates. The same is valid for HEOs, where the diverse metal (cation) parts (depending upon the metal type) function as active sites for the adsorption and conversion of molecular species (Chen *et al.*, 2018; Fracchia *et al.*, 2020a). The entropy-based phase stabilization in HEOs is assumed to aid efficient activation of lattice oxygen species, which along with their capability to accommodate large oxygen vacancies, further benefits the catalytic activity (Sun and Dai, 2021). Consequently, HEOs has been successfully used as catalysts for a wide variety of reactions, such as CO oxidation, aerobic oxidation of benzyl alcohol, oxidative desulfurization, hydrogen and oxygen evolution reactions, water-splitting, CO_2 hydrogenation, CH_4 combustion (Fig. 3b), etc., (Chen *et al.*, 2018; Li *et al.*, 2021; Sun and Dai,

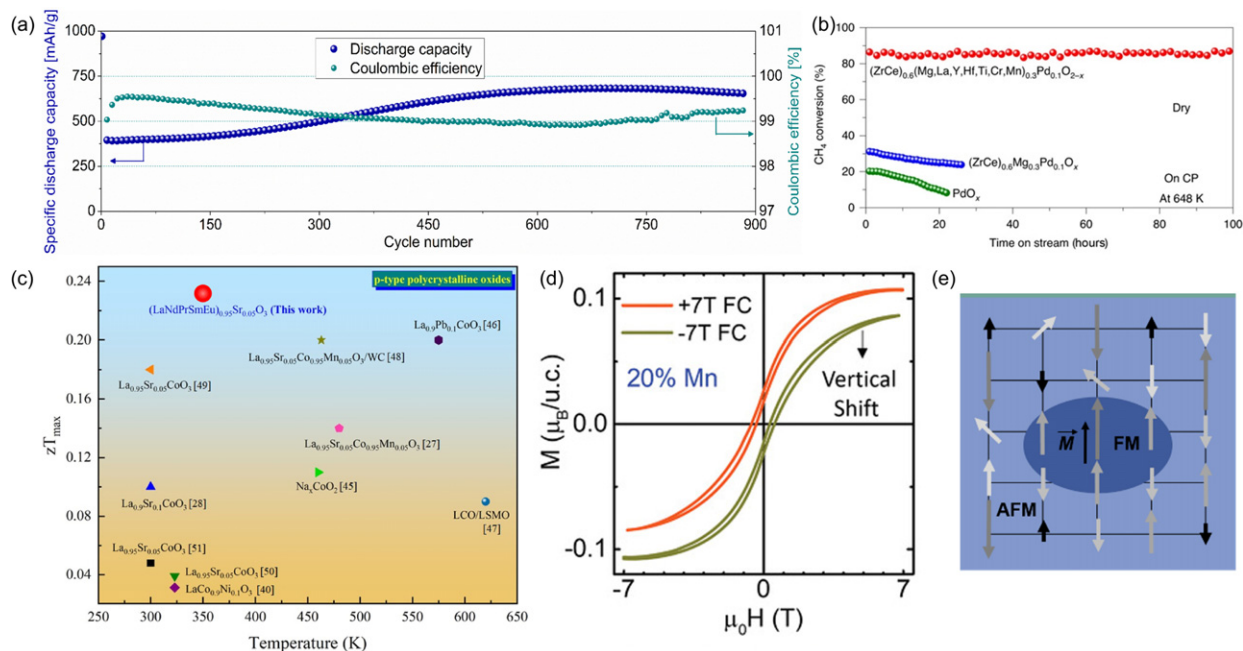


Fig. 3 Three different types of properties (electrochemical, thermal and magnetic) of HEOs are illustrated here. (a) represents the long-term cycling performance of $(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ at 200 mA g^{-1} vs. Li^+/Li in the potential window of 0.01–3 V, (b) shows the comparison of CH_4 oxidation performance of 10-MEO-PdO, $(\text{Zr,Ce})_{0.6}\text{Mg}_{0.3}\text{Pd}_{0.1}\text{O}_x$ (4-MEO-Pd), and PdO_x supported on carbon paper at 648K under dry conditions. (c) compares maximum figure of merit (zT_{max}) of $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_{0.95}\text{Sr}_{0.05}\text{CoO}_3$, red circle, with the reports in the literature for p -type polycrystalline oxide materials. (d) and (e) show the intrinsic vertical exchange bias stemming from a magnetic phase separation in $\text{La}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$. Reproduced from Sarkar, A., Wang, Q., Schiele, A., *et al.*, 2019. High-entropy oxides: Fundamental aspects and electrochemical properties. *Adv. Mater.* 31, 1806236. Available at: <https://doi.org/10.1002/adma.201806236>. Reproduced under the terms of the CC BY-NC-ND 4.0 license, copyright 2019, the authors, published by Wiley. Li, T., Yao, Y., Huang, Z., *et al.*, 2021. Denary oxide nanoparticles as highly stable catalysts for methane combustion. *Nat. Catal.* 4, 62–70. Available at: <https://doi.org/10.1038/s41929-020-00554-1>. Sun, Y., Dai, S., 2021. High-entropy materials for catalysis: A new frontier. *Sci. Adv.* 7. Available at: <https://doi.org/10.1126/sciadv.abg1600>. Reproduced under the terms of the CC BY-NC 4.0 license, copyright 2021, the authors, published by American Association for the Advancement of Science. Kumar, A., Dragoe, D., Berardan, D., Dragoe, N., 2022. Thermoelectric properties of high-entropy rare-earth cobaltates. *J. Mater.* Available at: <https://doi.org/10.1016/j.jmat.2022.08.001>. Reproduced under the terms of the CC BY-NC-ND license, copyright 2022, the authors, published by Elsevier B.V. Mazza, A.R., Skoropata, E., Sharma, Y., *et al.*, 2022. Designing magnetism in high entropy oxides. *Adv. Sci.* 9, 2200391. Available at: <https://doi.org/10.1002/advs.202200391>. Reproduced under the terms of the CC-BY 4.0 license, copyright 2022. Witte, R., Sarkar, A., Kruk, R., *et al.*, 2019. High-entropy oxides: An emerging prospect for magnetic rare-earth transition metal perovskites. *Phys. Rev. Mater.* 3, 034406. <https://doi.org/10.1103/PhysRevMaterials.3.034406>.

2021). Additionally, HEOs have also been used as support for catalysts, owing to their enhanced chemical and thermal stability (Xu *et al.*, 2020). Further details related to the use of HEOs for catalytic and electrochemical energy storage applications can be found in the following review articles (Ma *et al.*, 2021; Sun and Dai, 2021).

Thermal Properties

HEOs are known to exhibit enhanced thermal insulation compared to their constituent parent oxides counterparts (Banerjee *et al.*, 2020; Braun *et al.*, 2018; Gild *et al.*, 2018; Kumar *et al.*, 2022). In fact, these observations are consistent with earlier reports of suppressed thermal conduction in HEAs (Chuang *et al.*, 2016). The multication occupancy and the related local lattice distortions in HEOs are believed to underpin their significantly lower lattice thermal conductivity via enhanced phonon scattering. In addition to the lower thermal conductivity, some HEOs show superior high temperature stability along with retention of mechanical strength. Hence, they are often considered to be viable alternates for thermal barrier coatings. Another avenue where the ultralow thermal conductivity of HEO can be utilized is for the enhancement of the thermoelectric properties. The figure of merit (zT) in a thermoelectric material is inversely proportional to the thermal conductivity, thus lower thermal conductivity of HEOs is beneficial for higher zT . Apart from the thermal conductivity zT is directly proportional to the materials Seebeck coefficient (α) and electronic conductivity (σ). Recent studies have shown that α of HEOs can be enhanced compared to their conventional counterpart (Fig. 3c), thus further benefitting the zT (Kumar *et al.*, 2022). Although research along the direction of improving σ in oxides via HE-design approach is still lacking (and also to a certain extent counter-intuitive), the observations related to the enhancement of α and lowering the lattice thermal conductivity show promises for the use of HEOs as efficient thermoelectric materials.

Magnetic Properties

The dominant magnetic and correlated electronic features of HEOs largely resemble the isostructural conventional oxides, such as insulating antiferromagnetic (AFM) ground states in TM based rocksalt (Zhang *et al.*, 2019) or RE-TM based orthorhombic perovskites (Witte *et al.*, 2018), metallic ferromagnetic (FM) ground states in A-site disordered hole doped perovskite manganites (Sarkar *et al.*, 2022c), insulating paramagnetic ground states in RE based bixbyite or pyrochlore (Kinsler-Fedon *et al.*, 2020), and insulating ferrimagnetic (FiM) ground states in TM based spinels or hexaferrites (Sarkar *et al.*, 2022a; Vinnik *et al.*, 2019). These analogies make the generic magnetic properties in HEOs predictive from the viewpoint of crystallographic structure and composition to a certain extent. Nevertheless, there are prominent additional features which make the magnetic properties of HEOs unique. For instance, the presence of a stable long range magnetic ordering (AFM/FM/FiM) despite the extremely high chemical disorder is interesting (Witte *et al.*, 2019; Zhang *et al.*, 2019). Importantly, the feature that makes magnetism in HEOs quite special is the presence of multiple-principal cations on a given sub-lattice with varying metal-oxygen-metal bonds. This local diversity results in the creation of numerous, often competing, local constellations of exchange interactions, which consequently leads to magneto-electronic phase separation. This inherent magneto-electronic inhomogeneity in HEOs manifests itself through exotic phenomena such as intrinsic exchange bias in crystallographic single-phase HEOs (Mazza *et al.*, 2022; Witte *et al.*, 2019) (Fig. 3 d, e) and substantial colossal magnetoresistance surpassing the parent isostructural oxides counterparts (Sarkar *et al.*, 2022c). Essentially, the degree and nature of magneto-electronic inhomogeneity of HEOs can be further tailored via composition modulation and strain-engineering (Mazza *et al.*, 2022), which broaden the scope of achieving unique and enhanced magneto-electronic functionalities in HEOs.

On the one hand, the studies on a variety of functional properties have shown that the compositional flexibility while retaining the structural stability is one of the key features which makes the HEOs unique. On the other hand, searching the vast composition space of HEOs for finding the “sweet-spot” for property optimization remains as one of the major challenges in the field of HEO research. To tackle this challenge, high-throughput-based synthesis and analytical techniques have been extended to the HEO research field.

High-Throughput-Based Experimental Techniques

High-throughput (HT) based experimental techniques integrated with machine learning (ML) based automated data analysis are becoming increasingly important for materials screening in search for novel properties. In the case of HEOs materials, the traditional methodology based on “one-experiment at a time” faces additional limitations compared to conventional materials, due to the multidimensional composition space of HEOs. Recently, HT based experimental approach along with ML based data analysis technique has been used to study the phase stability and optical properties of fluorite-HEOs. In this specific case study (Velasco *et al.*, 2021), the cation ratios of fluorite-HEOs (having a pentanary composition space) were systematically varied using an automated HT-based wet chemical synthesis approach that allowed synthesis of ~100 samples per day. These 100 samples were further characterized in less than a week’s time using automated HT-X-ray diffraction for phase compositions, HT-scanning electron microscopy for chemical composition, HT-Raman spectroscopy for oxygen defect concentrations, and HT-Ultraviolet-Visible (UV-vis) spectroscopy for optical properties. Finally, ML models were trained to automatically analyze phase composition based on X-ray diffraction patterns, simplifying the data interpretation process. More recently, HT based approach has also been successfully applied to study the composition of spinel-HEOs for oxygen evolution reactions (Strotkötter *et al.*, 2022). In addition to these HT based experimental techniques and ML-based data analysis, computer-accelerated discovery of compositions (Kaufmann *et al.*, 2020; Pitike *et al.*, 2022) with new properties becomes equally important to explore the full potential of HEOs.

Conclusions

High entropy oxides (HEOs), despite their recent discovery in 2015, have gained significant research interest due to their unique structure stabilization mechanisms, ease of synthesis, and most importantly, their improved or nonconventional properties. The field of HEOs has already expanded to include many different classes of oxides, such as rocksalt, fluorite, perovskite, bixbyite, spinels, pyrochlores, delafossites, etc. Encouragingly, HEOs show a number of promising properties, for instance, enhanced electrochemical reversible energy storage capability, high catalytic activity, enhanced magnetoresistance and high thermal insulation. One of the major strengths of HEO-based materials is their ability to maintain phase purity despite their high compositional complexity, which offers an enormous composition space for property tailoring. On the other hand, the vast composition space of HEOs makes composition scouting challenging. Hence, high-throughput based experimental techniques along with machine learning-based materials discovery and data analysis are becoming key to rational design of HEOs for targeted applications.

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Ce³⁺ in Complex Garnets – Towards Red-Shifted Luminescence and Challenges Therein

Atul D Sontakke, Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, The Netherlands
Maths Karlsson, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Göteborg, Sweden

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Abstract

Ce³⁺ activated garnet hosts exhibit bright visible luminescence, and are widely used as phosphors and scintillating materials. In pursuit of Ce³⁺ containing red phosphors, garnets become an obvious choice. This is because of its inherently distorted dodecahedral dopant site that lead to superior crystal field, and its great freedom for complex compositional modification. Here, we present a detailed overview on how compositional modification of the garnet lattice impacts on the crystal field and centroid shift to effectively red-shift the Ce³⁺ emission. We also discuss the associated challenges that appear due to such compositional changes and present an outlook on future directives to achieve thermally stable Ce³⁺ containing red luminescent garnet phosphors.

Key Points

- The article presents an overview of Ce³⁺ doped garnets for orange-red emission.
- Previous efforts of crystal field and centroid shift tuning using complex compositional modification approaches are discussed.
- We also discuss the challenges in emission tuning on emission thermal stability, efficiency, etc.
- Finally an outlook is presented on achieving thermally stable orange-red emission of Ce³⁺ in garnet hosts.

Introduction

Garnets are an important class of inorganic mineral compounds with a simple cubic crystal structure, where the cations are accommodated in dodecahedral, octahedral and tetrahedral sites (Geiger, 2016). Its rigid cubic structure, impressive chemical and thermal stability and, of specific concern here, its availability of the convenient dodecahedral site for lanthanide doping make it an important choice for many optical applications. Several mainstream laser crystals, scintillators and phosphors are based on garnet compounds (Kaminskii, 1990; Dantelle *et al.*, 2020; Lin *et al.*, 2018). The prototypical garnet phosphor is yttrium aluminum garnet (Y₃Al₅O₁₂ or YAG) doped with cerium (YAG:Ce). Blasse *et al.* in the early 70' first demonstrated the yellow luminescent YAG:Ce, however, only after the invention of bright blue light emitting diodes (LEDs) and subsequent demonstration of white light generation using a blue LED plus YAG:Ce encapsulation by Nichia Inc., in 1996, YAG:Ce gained huge commercial interest (Blasse and Bril, 1967; Nakamura *et al.*, 1994; Bando *et al.*, 1996, 1998). YAG:Ce possesses an efficient, broadband yellow colored luminescence with a strong excitation band in the blue spectral region.

YAG is a typical example of the simple cubic garnet structure with *Ia3d* symmetry (Lin *et al.*, 2018). The general chemical formula of a perfect oxide garnet is A₃B₂C₃O₁₂, where A, B and C represent different individual cationic sites. The unit cell of the garnet structure is composed of 160 atoms and forms a body-centered cubic unit cell (Fig. 1(a)). In the unit cell, the A atoms occupy 8-fold dodecahedral coordination (24c sites), the B atoms occupy 6-fold octahedral coordination (16a sites) and the C atoms occupy four-fold tetrahedral coordination (24d sites). The oxygen atoms form the bridge between cations of different types and occupy tetrahedral (96 h) sites. The three dimensional network is composed of each octahedron connected to six tetrahedrons and the dodecahedral sites occupying interstitial spaces in the framework. In the garnet structure, the dodecahedral site is slightly distorted and therefore imposes a strong crystal field on the dopant ions (Fig. 1(b)). The Ce³⁺ 5d states exhibit unusually large energy splitting in the garnet lattice, which leads to its remarkably red-shifted emission properties over other compounds. In most compounds, the Ce³⁺ emission occurs in the ultraviolet (UV) to blue spectral region, but in garnets, the Ce³⁺ emission covers a broad range from the green to orange-red region (Yen *et al.*, 2007; Sontakke *et al.*, 2016). The emission color is (in part) determined by the chemical composition of the garnet lattice as both the centroid shift (ϵ_c) and crystal field splitting (Δ) are altered with the garnet composition. The centroid shift refers to the lowering of the Ce³⁺ 5d energy levels in a chemical environment due to a decrease in the interelectronic repulsion compared to its free ionic state. The crystal field splitting refers to the splitting of the 5d energy levels of Ce³⁺ ions into triply degenerate ²T_g and doubly degenerate ²E_g states, separated by the crystal field energy (Δ_o in octahedral field or Δ_c in cubic field). ²T_g and ²E_g are degenerate in perfect cubic symmetry but the tetragonal distortion to perfect cubic symmetry in the garnet lattice causes further splitting of the 5d state to five non-degenerate levels (5d₁ to 5d₅) (Lin *et al.*, 2018). In YAG, the doping of Ce³⁺ ions also leads to an increase in the site distortion, and thus the photoluminescence exhibits a systematic red-shift as the Ce³⁺ concentration increases. Ideally, the centroid shift follows the optical basicity (a combined effect of anion polarizability, bond covalency and cation electronegativity), whereas the crystal field is more complex and broadly follows the distortion of the dodecahedral site (Dorenbos, 2003).

The presence of three distinct cationic sites gives the garnet structure a remarkable flexibility in structural tuneability and thereby, the ability to systematically tune the luminescence properties. Xia and Meijerink (2017) made an extensive review on

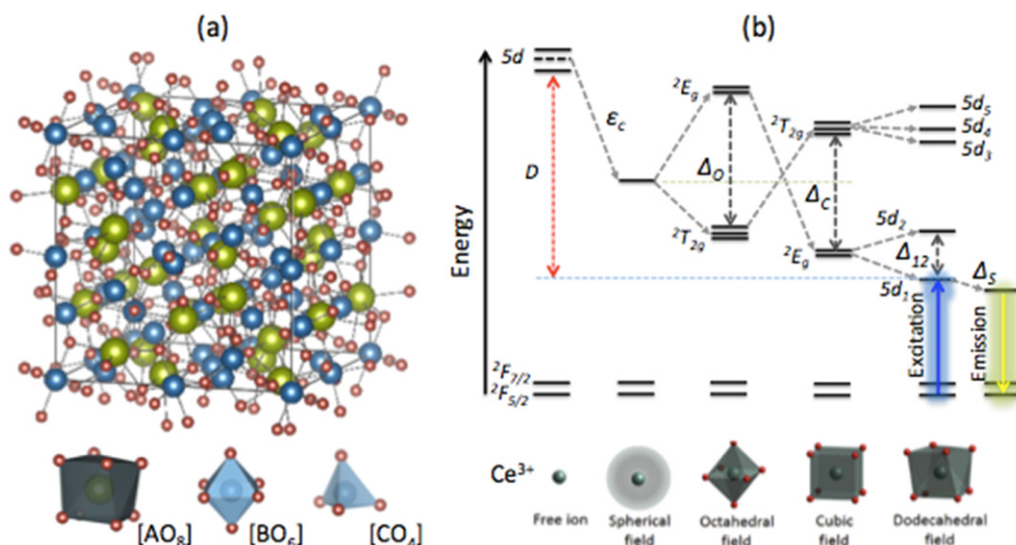


Fig. 1 Cubic crystal structure of the $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$ type garnet unit cell and the corresponding cation coordination polyhedra (a). The energy level splitting evolution of a Ce^{3+} ion from the free state to a dodecahedral lattice site in a garnet structure (b).

Ce^{3+} luminescence in garnet phosphors. It was pointed out that the Ce^{3+} photoluminescence is red-shifted compared to YAG if the dodecahedral cation is larger than yttrium and blue-shifted for smaller cations. Accordingly, the Ce^{3+} photoluminescence exhibits more yellowish color in, *e.g.*, TbAG (turbium aluminum garnet) and GdAG (gadolinium aluminum garnet), whereas LuAG (lutetium aluminum garnet) exhibits greenish luminescence. Likewise, cation substitutions at the octahedral and tetrahedral positions affect the photoluminescence properties. For example, the gallium substitution at the aluminum site systematically reduces the crystal field splitting and leads to a blue shift of the photoluminescence (Ueda *et al.*, 2011). In more complex compositions, it is possible to substitute divalent Ca, Mg, *etc.*, at the A site and tetravalent Si or Ge at C site as well as Sc, Y, *etc.*, at the B site to optimize the photoluminescence properties of Ce^{3+} ions in the garnet structure (Geiger, 2016; Sharma *et al.* 2018; Ueda and Tanabe, 2019). A partial nitridation of YAG was studied by Setlur *et al.* (2008a,b) using Si_3N_4 doping and which showed a red-shifted Ce^{3+} photoluminescence. Further, several researchers have reported a Mg^{2+} - Si^{4+} substitution in mixed YAG lattices and its effects on Ce^{3+} photoluminescence (Katelnikovas *et al.*, 2010; Setlur *et al.*, 2006). Robertson *et al.* (1981) showed that Gd substitution at the A site together with Mn^{2+} - Si^{4+} substitution at the B and C sites can lead to Ce^{3+} emission peaking at 615 nm. A Mg^{2+} - Si^{4+} couple on B and C sites can shift the Ce^{3+} emission to low energies due to stronger crystal field of the Ce^{3+} $5d$ states induced by replacement of Al^{3+} ion pairs at octahedral and tetrahedral site with Mg^{2+} and Si^{4+} respectively. These compositions provided initial design rules for Ce^{3+} red shifted emission in garnet lattices. However, a further red shift was limited due to garnet phase instability and lower emission efficiency. Later efforts then focused on the substitution of the dodecahedral A site with divalent alkaline earth metal ions, thus creating a more disordered site for the Ce^{3+} ions to lead to low energy red emission (Xia *et al.*, 2018; Ueda and Tanabe, 2019).

A red-shifted Ce^{3+} luminescence in the orange to red spectral region has great technological importance, especially in white light illumination applications. The current white LED devices employ red phosphors based on Eu^{2+} or Mn^{4+} , such as Eu^{2+} doped $(\text{Ca},\text{Sr})\text{SiAlN}_3$ and Mn^{4+} doped K_2SiF_6 , together with $\text{YAG}:\text{Ce}^{3+}$ as green-yellow phosphor. The red phosphor is necessary to achieve better color rendering and lower color temperature of illumination and thus to improve the color quality of LED devices (Smet *et al.*, 2011). At high excitation fluences, however, the red phosphors suffer from an emission droop (a deviation from the linear trend of excitation and emission intensities), primarily caused by the slower relaxation of Eu^{2+} and Mn^{4+} ions (van de Haar *et al.*, 2021; Setlur *et al.*, 2008a). The typical decay lifetime of Eu^{2+} emission is in the order of hundreds of nanoseconds to a few microseconds, and that of Mn^{4+} emission is of few milliseconds (spin-forbidden transition). Thus, the Eu^{2+} emission relaxation is about ten times slower than Ce^{3+} (emission decay time < 100 ns), whereas the spin-forbidden Mn^{4+} emission relaxation is several orders of magnitude slower. This significant difference in relaxation times suggests that the Eu^{2+} and Mn^{4+} ions are more susceptible to ground state depletion and excited state absorption/energy transfer (*i.e.*, upconversion) compared to Ce^{3+} . At high fluence excitation operation, this makes red emission ions difficult to compete with the fast response time of Ce^{3+} emission, and leads to a shift in correlated color temperature (CCT) of the white illumination (Hu *et al.*, 2021; Sijbom *et al.*, 2017; Setlur *et al.*, 2008a). This drawback limits the application of current red emission phosphors in high fluence conditions, where the phosphors are pumped using high power concentrated LEDs or laser diodes (LDs). A fast-response Ce^{3+} based red phosphor will thus help to realize and maintain the color quality in high fluence light sources. There have been two strategies, one to increase the crystal field and the other one focuses on the centroid shift of the Ce^{3+} $5d$ excitation levels to lower the energy. In the following of this review, we present an overview on the progress made in realizing Ce^{3+} red-shifted luminescence in garnet compounds and discuss an outlook of future directions.

Main Body

Ce^{3+} is one of the most efficient luminescent center in inorganic materials. Its fast response time (emission decay time < 100 ns) is widely employed in scintillators to improve the light yield as well as the screening accuracy in positron tomography (Dorenbos, 2005; Ronda and Srivastava, 2007). In phosphors, the Ce^{3+} ions show minimal droop when operated in high fluence conditions and therefore it is the only choice for LED based illumination sources. As discussed above, the luminescence properties of Ce^{3+} are mostly limited to the higher energy visible (UV to green) spectral region. In garnets, the high crystal field facilitates the red shifted Ce^{3+} photoluminescence towards the orange-red spectral range. However, it has been observed that the red-shift is limited and also such photoluminescence exhibits lower photoluminescence thermal quenching temperature (Ueda and Tanabe, 2019). A direct relation between red shift and thermal quenching is difficult to establish; however, it is possible that in ceratin compositions, the red shift is accompanied with a large offset between the ground and excited state configuration leading to a low crossover energy. Such large offset is commonly observed in hosts with less rigid structure having lower Debye temperature (Amachraa *et al.*, 2020). There have been two prominent mechanisms established for Ce^{3+} emission thermal quenching: the configuration crossover between excited and ground state and the thermal ionization of excited state electron to the conduction band of the host lattice. The former one depends on the excited state configuration offset, whereas the latter one is governed by the energy difference between excited state and the bottom of the conduction band (Fig. 2). In rigid phosphor hosts with a high Debye temperature, the thermal quenching by configuration crossover is less probable, but there are few exceptions to this behavior and they usually fall in the category of thermal quenching by electron ionization. This mechanism may be distinguished using the relative difference between activation energies for thermal quenching processes (Fig. 2). The individual activation energies can be approximated based on the position of conduction band energy with respect to the Ce^{3+} excited state energy for the thermal ionization process, and from the emission Stokes shift, which also reflects the extent of ground and excited state minima offset for configuration crossover. It is evident that a large Stokes shift can lead to a lower energy red-shifted emission, however, such emission can be more prone to thermal quenching following configuration crossover relaxation. It is therefore necessary to find a suitable optimization between emission energy and Stokes shift.

Table 1 summarizes the Ce^{3+} optical properties in some prominent garnet compounds. It is evident that the garnet structures having Mg or Ca at the dodecahedral A site leads to significantly red-shifted photoluminescence compared to YAG and other regular garnets having Ln ions as dodecahedral A cations. There are a few compositions where Mg^{2+} - Si^{4+} pairs help achieve orange-red Ce^{3+} photoluminescence in regular aluminate garnets with Ln ions at the octahedral site. In addition, the partial nitridation of YAG ($\text{Y}_3\text{Al}_{5-x}\text{Si}_x\text{O}_{12}\text{N}_x$) shifts the emission to the red spectral region. The nitride anions increase the covalent character of the metal-anion bonds and thus lowers the centroid energy. Owing to the same anion nature in pure oxide garnets, the centroid energy shift is less and it becomes relatively less important when deciding the emission energy (Dorenbos, 2003). Here, the crystal field plays a major role (Fig. 3). Ueda and Tanabe (2019) pointed on that the crystal field splitting ($\epsilon_{\text{cfs}} = 5d_5 - 5d_1$) exhibits a direct relation with the splitting of the lowest two $5d$ states (Δ_{12}), and the later can be used as a measure of the magnitude of the crystal field splitting. Accordingly, with increased Δ_{12} , a larger red shift (D) is expected. The plot of the $5d$ energy

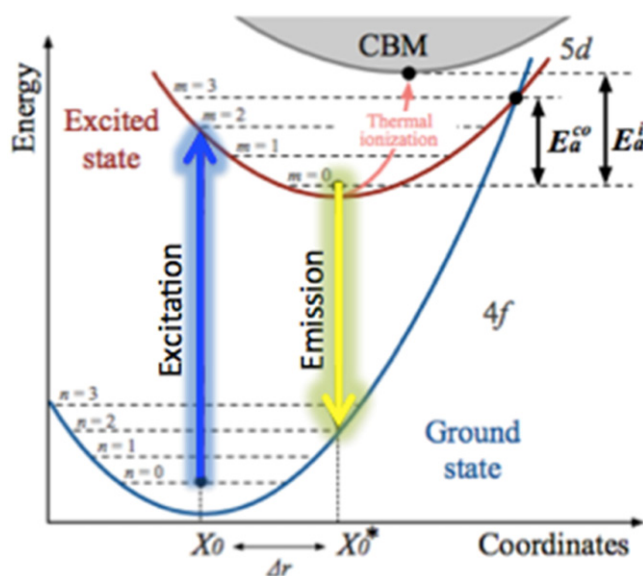


Fig. 2 Schematic configuration coordinate diagram of the Ce^{3+} energy levels in a host lattice. The excited state minimum shifts from that of ground state minimum due to modified configuration rearrangement caused by the excited electron in the $5d$ state. The configuration offset (Δr) presents the extent of offset and depends on the host lattice. The E_a^{co} and E_a^i represent the activation energies for configuration crossover and thermal ionization of excited state electrons to the conduction band minimum (CBM), respectively. Adapted from Amachraa, M., Wang, Z., Tang, H., *et al.*, 2020. Unified theory of thermal quenching in inorganic phosphors. arXiv:1910.12420v2[cond-mat.mtrl-sci].

Table 1 Ce³⁺ activated garnet compounds and the ⁵d₁ ← ⁴f excitation peak wavelengths, λ_{ex} (nm), ⁵d₁ → ⁴f emission peak wavelength, λ_{em} (nm), photoluminescence thermal quenching temperature at 50% intensity (T_{50%}) and the Stokes shift (ΔS). The Stokes shift is derived from the peak emission and excitation energies

Compound	λ_{ex} (nm)	λ_{em} (nm)	T _{50%} (K)	ΔS (cm ⁻¹)	References
	5d ₂	5d ₁			
Y ₃ Al ₅ O ₁₂ :Ce ³⁺	340	460 532	640	2942	Lin <i>et al.</i> , 2018
Y ₃ Al ₄ GaO ₁₂ :Ce ³⁺	346	450 519	583	2954	Ueda <i>et al.</i> , 2011
Y ₃ Al ₃ Ga ₂ O ₁₂ :Ce ³⁺	347	446 508	491	2736	Ueda <i>et al.</i> , 2011
Y ₃ Al ₂ Ga ₃ O ₁₂ :Ce ³⁺	349	435 505	344	3186	Ueda <i>et al.</i> , 2011
Y ₃ Al ₁ Ga ₄ O ₁₂ :Ce ³⁺	355	430 497	301	3135	Ueda <i>et al.</i> , 2011
Gd ₃ Al ₅ O ₁₂ :Ce ³⁺	337	470 560	405	3419	Xie <i>et al.</i> , 2012
Gd ₃ Al ₄ GaO ₁₂ :Ce ³⁺	339	459 554	406	3735	Kamada <i>et al.</i> , 2011
Gd ₃ Al ₃ Ga ₂ O ₁₂ :Ce ³⁺	340	448 540	410	3802	Kamada <i>et al.</i> , 2011
Gd ₃ Al ₂ Ga ₃ O ₁₂ :Ce ³⁺	344	441 532	320	3878	Kamada <i>et al.</i> , 2011
Gd ₃ AlGa ₄ O ₁₂ :Ce ³⁺	347	437 529	175	3980	Kamada <i>et al.</i> , 2011
Tb ₃ Al ₅ O ₁₂ :Ce ³⁺	330	470 553	–	3193	Markovskiy <i>et al.</i> , 2021
Lu ₃ Al ₅ O ₁₂ :Ce ³⁺	348	448 505	800	2519	Ivanovskikh <i>et al.</i> , 2013
Gd ₂ YAl ₅ O ₁₂ :Ce ³⁺	337	467 565	408	3714	Asami <i>et al.</i> , 2019
GdY ₂ Al ₅ O ₁₂ :Ce ³⁺	339	463 560	454	3741	Asami <i>et al.</i> , 2019
Y ₃ Sc ₂ Al ₃ O ₁₂ :Ce ³⁺	348	443 503	533	2692	Ueda <i>et al.</i> , 2013
Y ₃ Sc ₂ Al ₂ GaO ₁₂ :Ce ³⁺	349	427 502	483	3498	Ueda <i>et al.</i> , 2013
Y ₃ Sc ₂ AlGa ₂ O ₁₂ :Ce ³⁺	350	420 500	410	3809	Ueda <i>et al.</i> , 2013
Ca ₃ Sc ₂ Si ₃ O ₁₂ :Ce ³⁺	308	432 505	900	3346	Sharma <i>et al.</i> , 2018
Ca ₃ Y ₂ Ge ₃ O ₁₂ :Ce ³⁺	312	425 495	265	3327	Cui <i>et al.</i> , 2021
Sr ₃ Y ₂ Ge ₃ O ₁₂ :Ce ³⁺	297	433 530	320	4226	Pasinski <i>et al.</i> , 2015
Mg ₃ Y ₂ Ge ₃ O ₁₂ :Ce ³⁺	320	463 555	283	3580	Jiang <i>et al.</i> , 2010
Mg ₃ Y ₂ Ge _{2.7} Si _{0.3} O ₁₂ :Ce ³⁺	318	466 580	–	4217	Jiang <i>et al.</i> , 2010
Mg ₃ Y ₂ Ge _{2.1} Si _{0.9} O ₁₂ :Ce ³⁺	314	468 585	–	4273	Jiang <i>et al.</i> , 2010
Mg ₃ Y ₂ Ge _{1.5} Si _{1.5} O ₁₂ :Ce ³⁺	310	470 590	300	4327	Jiang <i>et al.</i> , 2010
Mg ₃ Y ₂ Ge _{0.9} Si _{2.1} O ₁₂ :Ce ³⁺	308	474 604	–	4540	Jiang <i>et al.</i> , 2010
Lu ₂ Mg ₂ Al ₂ Si ₂ O ₁₂ :Ce ³⁺	327	436 575	495	5544	Zhou <i>et al.</i> , 2017
Lu ₂ CaMg ₂ (SiO ₄) ₃ :Ce ³⁺	322	473 605	475	4612	Setlur <i>et al.</i> , 2006
MgY ₂ Al ₄ SiO ₁₂ :Ce ³⁺	320	452 566	–	4456	Pan <i>et al.</i> , 2016
Y ₃ Mg ₂ AlSi ₂ O ₁₂ :Ce ³⁺	335	475 600	385	4386	Katelnikovas <i>et al.</i> , 2009
MgY ₂ Al ₃ Si ₂ O ₁₁ N:Ce ³⁺	320	450 570	495	4678	Pan <i>et al.</i> , 2018
Y ₃ Al _{5-x} Si _x O _{12-x} N _x :Ce ³⁺	333	470 620	400	5150	Setlur <i>et al.</i> , 2008b
Lu ₃ Al _{5-x} Si _x O _{12-x} N _x :Ce ³⁺	345	450 550	405	4040	Liu <i>et al.</i> , 2015

levels with red shift (*D*) in Fig. 3 depicts that the garnets having Ln ions at the dodecahedral A site and Al or Ga type trivalent ions at the B and C sites exhibit a steady trend between Δ₁₂ and the red shift (*D*). In case of garnets with alkaline earth metal ions at the A site and Si or Ge at the C site, the crystal field splitting is often larger compared to the respective same *D* value for regular garnets having trivalent cations at the C sites.

The increased crystal field due to alkaline earth metal ions in garnets is interesting to achieve a red shifted emission. Although some of them are difficult to achieve in pure phase and may accompany some impurities, it is widely being explored to study the Ce³⁺ photoluminescence properties. A significant photoluminescence shift could be achieved in Y₃Mg₂AlSi₂O₁₂:Ce³⁺ by Mg²⁺-Si⁴⁺ substitution at Al³⁺ pairs at octahedral and tetrahedral sites (Fig. 4) (Katelnikovas *et al.*, 2010). In Mg₃Y₂Ge_{3-x}Si_xO₁₂ inverse garnets, Jiang *et al.* (2010) showed that increasing the Si content further increases the energy splitting and gives red shifted photoluminescence (Fig. 5). The effect is claimed to be due to the smaller size of Si over Ge. This leads to increased crystal field and is suggested to be the same effect as the replacement of Al by Ga in YAGG (yttrium aluminum gallium garnet). The structural disorder at the Ce³⁺ site in Mg₃Y₂Ge_{3-x}Si_xO₁₂ is also claimed to be responsible for the red shifted emission. For 0%–70% Si substitution, the photoluminescence peak shifts from 580 nm to 605 nm with the photoluminescence quantum yield increasing from a few percent to more than 50%. In a similar Si-Ge substitution report by Setlur *et al.* (2006), the authors showed the improved photoluminescence properties in silicate phase, Lu₂CaMg₂(SiO₄)₃. The authors also indicated the presence of multiple non-equivalent sites of Ce³⁺ in Lu₂CaMg₂(SiO₄)₃ due to the disorder on the dodecahedral A site occupied by Lu and Ca ions. The energy transfer between the Ce³⁺ ions at different sites causes a reddish emission at around 600 nm under an excitation at 475 nm. This is indeed ideal for blue LED excitation.

The complexity of site disorders and associated presence of several Ce³⁺ sites may partially be responsible to a higher average Stokes shift in such mixed alkali metal ion garnets (Table 1). The typical Stokes shift of Ce³⁺ transitions in garnets is around 2200–3500 cm⁻¹. It may also be possible that the mixed structure allows large configurational offset to cause large Stokes shift. In

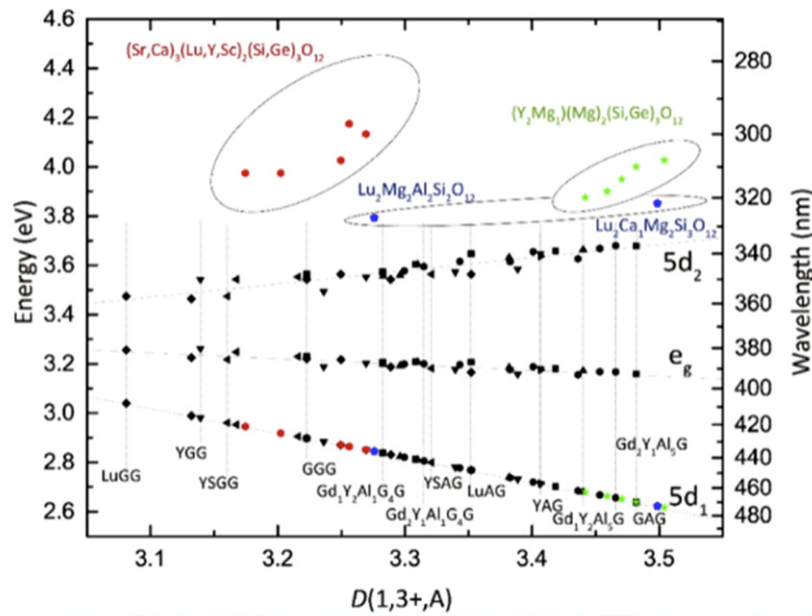


Fig. 3 Ce³⁺ energy levels in the first two excited states ($5d_1$ and $5d_2$) and the centroid energy of the $5d_1$ and $5d_2$ states (e_g) in garnets as a function of the red-shift $D(1, 3+, A)$. Used with permission from Ueda, J., Tanabe, S., 2019. (INVITED) Review of luminescent properties of Ce³⁺-doped garnet phosphors: New insight into the effect of crystal and electronic structure. Opt. Mater. X 1, 100018.

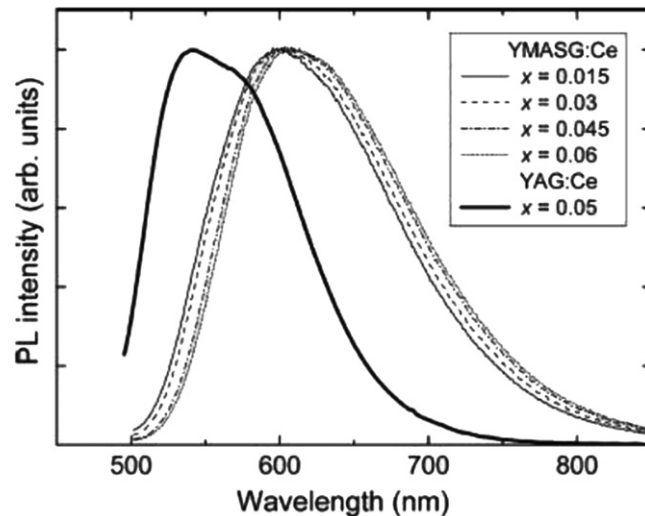


Fig. 4 Normalized photoluminescence spectra of $\text{Y}_3\text{Mg}_2\text{AlSi}_2\text{O}_{12}:\text{Ce}^{3+}$ (YMASG:Ce) with different Ce³⁺ doping concentrations. The YAG:Ce spectrum is provided for comparison. Used with permission from Katelnikovas, A., Bareika, T., Vitta, P., *et al.*, 2010. $\text{Y}_{3-x}\text{Mg}_2\text{AlSi}_2\text{O}_{12}$: Phosphors – Prospective for warm-white light emitting diodes. Opt. Mater. 32 (9), 1261–1265.

most garnets, including YAG, YAGG, $\text{Lu}_2\text{CaMg}_2(\text{SiO}_4)_3$, *etc.*, the thermal quenching of Ce³⁺ emission is ascribed to thermal ionization of the excited state electron to the conduction band; however, in $\text{Mg}_3\text{Y}_2\text{Ce}_{3-x}\text{Si}_x\text{O}_{12}$, the presence of configuration crossover between the excited state and ground state is proposed as an additional cause of thermal quenching of luminescence. Thus a further red shift in emission in such compositions, either by increased crystal field or by configuration offset can be limited as this will lead to an increase in the crossover probability (Ueda *et al.*, 2011). Here, a partial nitridation of the garnet network can be of much help to shift the Ce³⁺ photoluminescence towards the red wavelength region and still maintain a good thermal stability and photoluminescence efficiency. Pan *et al.* (2018) reported on the Ce³⁺ emission in $\text{MgY}_2\text{Al}_2\text{Si}_2\text{O}_{11}\text{N}$, which exhibits a peak photoluminescence intensity at approximately 570 nm and a thermal quenching temperature as high as 494 K. This is better than the GdAG:Ce garnet, which shows a much poorer thermal stability in this spectral region (Xie *et al.*, 2012). An earlier report on partial nitridation of the YAG lattice using Si_3N_4 doping revealed a photoluminescence peak intensity at approximately 620 nm

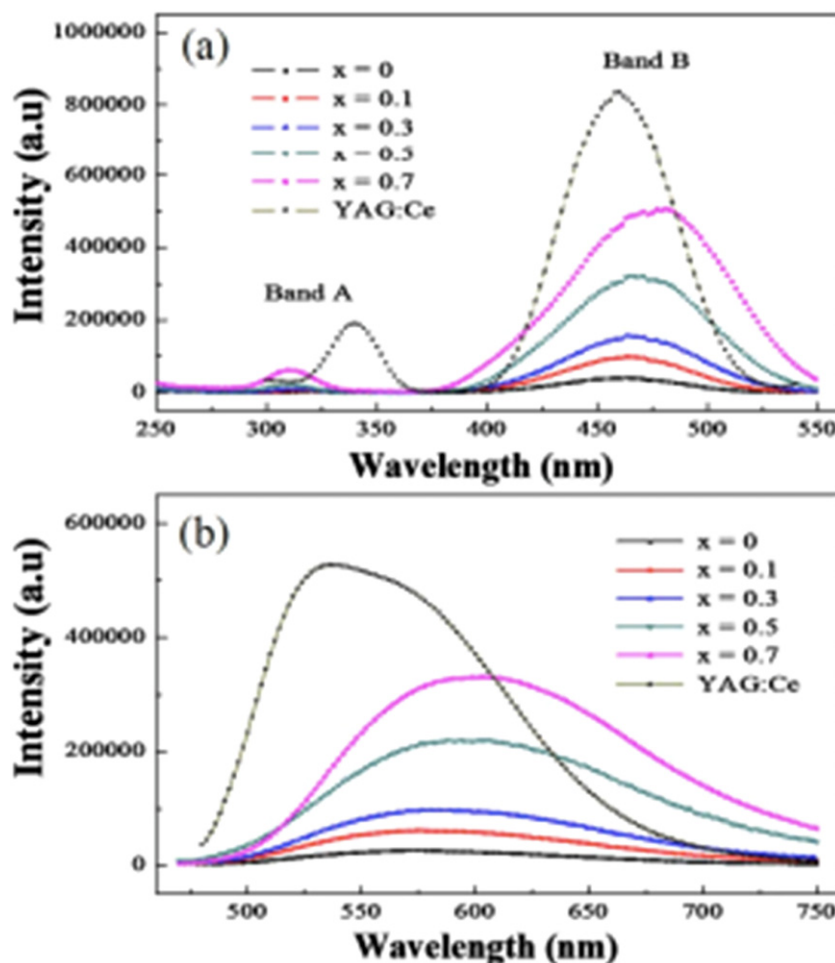


Fig. 5 Photoluminescence excitation (a) and emission (b) spectra of $\text{Mg}_3\text{Y}_{1.97}(\text{Ge}_{1-x}\text{Si}_x)_{12}:0.03\text{Ce}^{3+}$ garnet compounds and YAG:Ce. The excitation in (b) was at 460 nm. Used with permission from Jiang, Z.Q., Wang, Y.H., Wang, L.S., 2010. Enhanced yellow-to-orange emission of Si-doped $\text{Mg}_3\text{Y}_2\text{Ge}_3\text{O}_{12}:\text{Ce}^{3+}$ garnet phosphors for warm white light-emitting diodes. *J. Electrochem. Soc.* 157, J155–J158.

(Fig. 6) (Setlur *et al.*, 2008b). Although the nitridation causes a slight decrease in thermal stability compared to YAG, the benefits of a red shift relatively outperforms the similar effect obtained in mixed oxide garnets.

The partial nitridation of the garnet network has been reported in several recent works. Wang *et al.* (2012) showed the effect of different nitridation precursors and fluxes on the photoluminescence properties of $\text{Y}_3\text{Al}_{5-x}\text{Si}_x\text{O}_{12-x}\text{N}_x:\text{Ce}^{3+}$. Asami *et al.* (2019) and Ahn and Kim (2016) reported on the nitridation of $(\text{Y,Gd})_3\text{Al}_{5-x}\text{Si}_x\text{O}_{12-x}\text{N}_x$ and $\text{Lu}_3\text{Al}_{5-x}\text{Si}_x\text{O}_{12-x}\text{N}_x$, respectively. The benefit of nitrides is its ability to maintain a high lattice rigidity, which helps to avoid thermal quenching of luminescence by configuration crossover mechanism. Although, the Stokes shift in Table 1 suggests the values in the range of $4500\text{--}5000\text{ cm}^{-1}$, but, this can be due to the presence of a disordered oxynitride coordination causing non-equivalent dopant sites and energy transfer among them. A similar anionic inhomogeneity resulting in multiple non-equivalent dopant sites has recently been demonstrated in $\alpha\text{-SiAlON}$ oxynitride host (Sontakke *et al.*, 2021).

Future Directions

Over several years, Ce^{3+} spectroscopy in garnets has been extensively carried out in the search of efficient fast responsive phosphors. In most of these investigations, the main focus was attributed to the oxide compositions and solid solutions thereof determining the Ce^{3+} luminescence properties and subsequent emission red-shift towards the orange-red emitting phosphors. A vast amount of oxynitride garnets are still unexplored and thus shows a large potential to realize an efficient red emitting phosphor. The combined effect of crystal field and centroid shift tuning would be an interesting strategy to follow up. The incorporation of nitride anions in garnets can be challenging but not impossible. We have witnessed the success of Eu^{2+} doped nitride and oxynitride phosphors, which helped to shift the Eu^{2+} emission to the red to near infrared spectral range. Moreover, the nitride and oxynitride phosphors possess high stability towards thermal, chemical and optical effects.

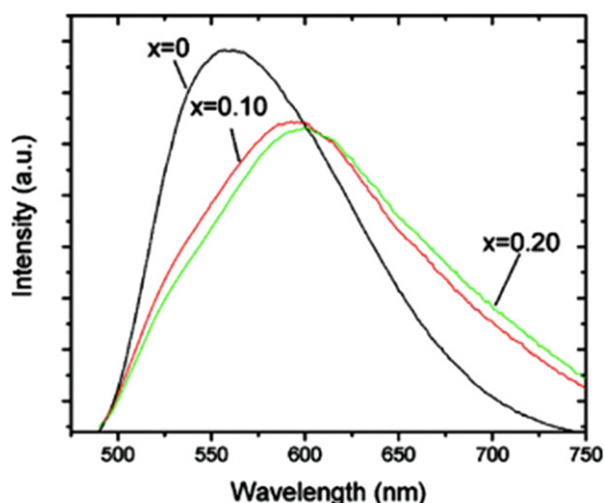


Fig. 6 Photoluminescence spectra of $(\text{Y}_{0.97}\text{Ce}_{0.03})_3\text{Al}_{5-x}\text{Si}_x\text{O}_{12-x}\text{N}_x$ at room temperature, as excited at 470 nm. Used with permission from Setlur, A.A., Heward, W.J., Hannah, M.E., Happek, U., 2008b. Incorporation of $\text{Si}^{4+}-\text{N}^{3-}$ into Ce^{3+} -doped garnets for warm white LED phosphors. *Chem. Mater.* 20, 6277–6283.

Conclusions

In summary, we have given an overview on efforts being made to red-shift the Ce^{3+} photoluminescence towards the orange-red spectral range in garnet lattices. The strategy of incorporating divalent alkaline metal cations at the A site or $\text{Mg}^{2+}-\text{Si}^{4+}$ pair at the B and C sites, respectively, proved helpful to increase the crystal field effect, whereas the mixed anionic oxynitride compositions incorporated higher centroid shift, thus causing a large red shift (*D*) of the excited state energy. It is argued that a combined optimization of both increased crystal field and centroid shift effect should be approached to achieve thermally stable Ce^{3+} orange-red emission in garnet host phosphor.

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High Temperature Superconductors

Pietro Carretta and Giacomo Prando, Department of Physics, University of Pavia, Pavia, Italy

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Abstract

In this article, we describe the phenomenology of the superconducting state in condensed matter. We start introducing the main properties and experimental signatures of conventional superconductivity in elemental metals and metallic alloys. Next, we focus on unconventional high temperature superconductivity in copper oxides and on the highly complex electronic phase diagram of these materials. Finally, we review the appearance of high temperature superconductivity in other classes of oxides such as bismuthates and nickelates.

Nomenclature

B	Magnetic flux density
e	Elementary electric charge
h	Planck's constant
H	Magnetic field strength
H_c	Critical magnetic field strength
H_{c1}	Lower critical magnetic field strength
H_{c2}	Upper critical magnetic field strength
J_c	Critical current density
t	Mott-Hubbard hopping kinetic energy
T	Temperature
T_c	Superconducting critical temperature
T_N	Antiferromagnetic critical temperature
T^*	Pseudogap characteristic onset temperature
U	Mott-Hubbard repulsion energy
x	Charge-doping fraction
x_{opt}	Charge-doping fraction at optimal doping
Δ	Superconducting energy gap
Δ_{CT}	Charge-transfer energy
λ_L	London penetration depth
μ_0	Vacuum permeability
Ψ_{sc}	Superconducting wavefunction
ξ_{GL}	Ginzburg-Landau coherence length
Φ_0	Magnetic flux quantum
ρ	Electrical resistivity

Key Points

- Definition of the main properties of the superconducting state.
- Presentation of conventional superconductivity as realized in some elemental metals.
- Discussion of the main crystallographic and electronic properties of copper-based oxides.
- Presentation of copper oxides as prototypes of unconventional superconductors.
- Description of the main features of the characteristic electronic phase diagram of cuprates.
- Presentation of other families of oxide superconductors.

In this article, we describe the main phenomenological aspects of high temperature superconductivity as realized in copper-based oxides. We start from an overview of the defining properties of the superconducting state in Section “Conventional Superconductivity” and specialize the discussion to the so-called conventional superconductivity observed, among others, in some elemental metals (Section “Conventional Superconductors”). We then move to Section “Copper Oxides” where we summarize the characterizing crystallographic and electronic features of cuprates. In Sections “Unconventional Superconductivity” and “Phase Diagram” we come to the main phenomenological properties of cuprates, starting from the unconventional superconducting state developing therein and describing the rich and complex electronic phase diagram characteristic of these materials. Finally, we

discuss the observation of high temperature superconductivity in other families of oxides, i.e., bismuthates and nickelates (Section “Superconductivity in other Oxides”).

Conventional Superconductivity

The sudden vanishing of the electrical resistivity ρ below a critical temperature T_c and for current densities lower than a critical value J_c epitomizes the development of superconductivity in condensed matter. The first observation of this phenomenon dates back to 1911 and was made by Heike Kamerlingh Onnes in mercury, where $T_c \simeq 4.2$ K (both T_c and J_c are material-dependent quantities) – see [Van Delft and Kes \(2010\)](#) and [Van Delft \(2012\)](#) for historical accounts of the discovery. However, even most striking manifestations of the superconducting state belong to the realm of magnetism. In particular, superconductors behave as perfect diamagnets in that they totally shield their bulk from externally applied magnetic fields H provided that $H < H_c$, where H_c is another material-dependent critical quantity. This latter phenomenon, dubbed Meissner-Ochsenfeld effect, characterizes superconductivity as an equilibrium thermodynamical phase of matter, going beyond what is implied by zero-resistivity alone – see [De Gennes \(1999\)](#) and [Schrieffer \(1999\)](#).

The magnetic field–temperature (H - T) phase diagram of the so-called type I superconductors is then dichotomous, with a sharp crossover between a Meissner-Ochsenfeld state and a non-superconducting, metallic “normal” phase – see the left-hand panel of [Fig. 1](#). A richer phenomenology is observed in the H - T phase diagrams of type II superconductors, where a mixed (or Shubnikov) phase separates the Meissner-Ochsenfeld and normal states – see the right-hand panel of [Fig. 1](#). In particular, within the mixed state the external magnetic field partially penetrates the superconductor in the form of tube-like filaments (or “vortices”) carrying a quantized unit of magnetic flux

$$\Phi_0 = \frac{h}{2e} \simeq 2.0678 \times 10^{-15} \text{ Wb} \quad (1)$$

where h is Planck's constant and e is the electron charge. Two critical magnetic fields enclose the mixed state: the lower critical field H_{c1} separates the Meissner-Ochsenfeld phase from the mixed phase and the upper critical field H_{c2} divides the mixed and the normal states.

The distinction between type I and II superconductors is based on the values of two characteristic material-dependent lengths, λ_L and ξ_{GL} . The London penetration depth λ_L quantifies the distance over which the external magnetic field is effectively screened. Typical values for λ_L in metallic superconductors are in the order of 10^{-8} – 10^{-7} m and are affected by the density of impurities. On the other hand, the Ginzburg-Landau coherence length ξ_{GL} is the characteristic distance required by the quantum superconducting wavefunction Ψ_{sc} to recover its bulk value from an interface with a normal material (where $\Psi_{sc} = 0$). It turns out that ξ_{GL} has a more extended range of variability among metallic superconductors if compared to λ_L , taking characteristic values from 10^{-9} m up to almost 10^{-6} m. In 1957, Aleksey Alekseevich Abrikosov demonstrated that type I and II superconductors are defined by the conditions $\lambda_L/\xi_{GL} < 1/\sqrt{2}$ and $\lambda_L/\xi_{GL} > 1/\sqrt{2}$, respectively – see [Abrikosov \(1957\)](#).

The above en-passant mention of Ψ_{sc} implies the purely quantum nature of superconductivity. In particular, all the charged carriers of the superconducting state are described by a single coherent wavefunction, characterized by a well-defined phase value. This description is well captured by the first successful microscopic theory of superconductivity, formulated in 1957 by John Bardeen, Leon N. Cooper and John Robert Schrieffer – see [Bardeen et al. \(1957\)](#). The most spectacular manifestation of the macroscopic nature of Ψ_{sc} is the observation of interference effects for two juxtaposed superconductors separated by a thin insulating layer. These phenomena are referred to as Josephson effects and their robustness has been exploited to define the metrological voltage quantum standard – see [Barone and Paternò \(1982\)](#). These arguments make it clear that the elementary

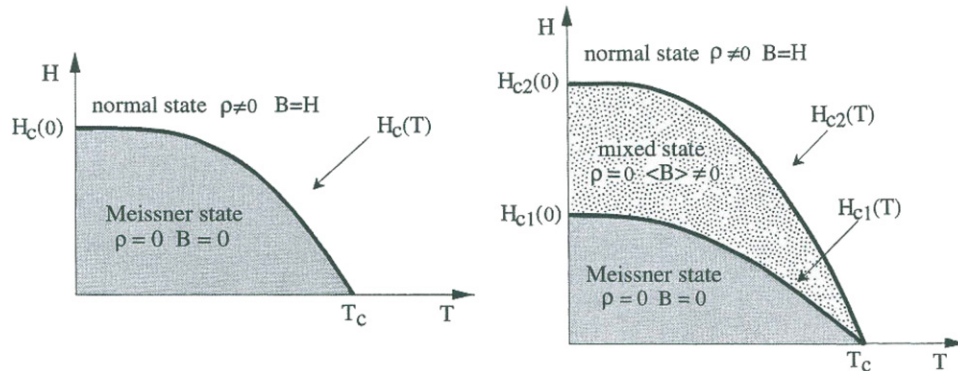


Fig. 1 Representative H - T phase diagrams for type I and type II superconductors (left-hand and right-hand panels, respectively). The figures are adapted from Grosso, G., Pastori Parravicini, G., 2000. Solid State Physics. San Diego, London: Academic Press.

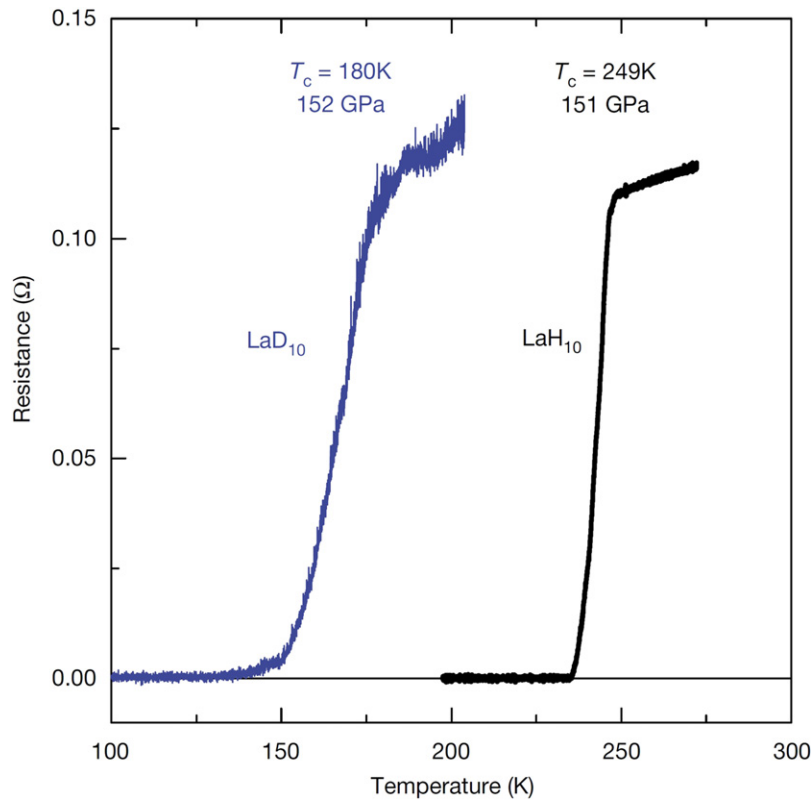


Fig. 2 Isotope effect on the superconducting resistive transition of LaH_{10} after the substitution of hydrogen with deuterium (D). The figure is reproduced from Drozdov, A.P., Kong, P.P., Minkov, V.S., *et al.*, 2019. Superconductivity at 250 K in lanthanum hydride under high pressures. *Nature* 569, 528–531.

charge carriers in superconductors cannot be single electrons, due to the electron's fermionic character. Several experimental evidences suggest instead that electrons in superconductors pair up in bound states – the so-called Cooper pairs – and this ultimately allows the development of quantum coherence to a macroscopic level. This fact is directly reflected in the appearance of twice the electron charge in the expression for Φ_0 (see Eq. (1)), but several additional experimental evidences support this scenario. Among these, the most important is the observation of an energy gap Δ in the excitation spectrum, with a typical value in the order of 10^{-4} eV (corresponding to $\sim 10^{-23}$ J) for metallic superconductors, which can be understood as the energy cost required to split a Cooper pair in two unbound fermionic entities dubbed Bogoljubov quasi-particles – see [Bogoljubov, 1958](#); [Valatin, 1958](#) and [Venema *et al.*, 2016](#). Experimental quantities directly influenced by Δ range from the specific heat for $T \ll T_c$ to tunneling currents, and from the absorption of electromagnetic radiation to the spin-lattice relaxation rate in nuclear magnetic resonance (NMR) – see [Tinkham \(2004\)](#) and [Mangin and Kahn \(2017\)](#).

A microscopic mechanism for the generation of a bound electron-electron pair in a solid was proposed by Herbert Frölich already in 1950. In particular, based on this model, the electrons interact directly via the Coulomb repulsion but they also attract each other via an indirect interaction mediated by the quantized lattice vibrations, i.e., phonons. In this sense, the lattice contributes in a fundamental way to the electronic properties of superconductors, therefore invalidating the Born-Oppenheimer approximation which separates the nuclear and electronic degrees of freedom. The main experimental evidence suggesting the direct involvement of the lattice in the phenomenon of superconductivity is the so-called isotope effect, i.e., the dependence of T_c on isotopic substitutions modifying the nuclear mass while preserving the electronic properties essentially unmodified (see [Fig. 2](#)). It should be remarked that a strong electron-phonon interaction is simultaneously detrimental for the normal metallic phase – implying high resistivity values – and beneficial for the realization of robust superconductivity. The opposite argument explains why good metals, which are characterized by low resistivity values in the normal phase, normally do not superconduct.

Conventional Superconductors

The research activity on superconductors is chiefly driven by the attempt to maximize their main figure of merit, i.e., the critical temperature T_c , towards the Holy Grail of a dissipationless electrical conductor at ambient temperature. The microscopic theory by Bardeen, Cooper and Schrieffer (BCS) has been a major leap forward in this respect, even though its predictive power has been severely limited for long time by the lack of computational tools suited for its ab-initio implementation. For this reason, the empirical rules formulated by Bernd Theodor Matthias were the main guiding light for the researchers towards the discovery of

new, more and more performing superconductors during the 1960s and 1970s – see [Matthias et al. \(1963\)](#). Based on Matthias' prescriptions, the materials suited to host superconductivity should show high crystalline symmetry (possibly cubic) and a normal metallic phase with high density of states at the Fermi energy – additionally, magnetic ions and oxygen should be avoided.

Most of the superconductors discovered before 1986 agree well with the rules put forward by Matthias. Among these, the simplest are elemental metals such as Hg, Al, In, Sn, Pb and Nb (as already mentioned above, good metals such as Cu, Ag and Au do not superconduct because of their weak characteristic electron-phonon coupling). Among the elemental metals, the typical T_c values are around few Kelvin degrees, the highest value ~ 9.5 K being reported for Nb. Such low critical temperatures require liquid helium as cooling medium, which is inconvenient in terms of costs and (more and more often scarce) availability. More severe limitations to the technological applications of elemental metals come from the low critical magnetic fields H_c . The typical values for this quantity at zero-temperature are around a tenth of Tesla, with Nb holding again the highest value $\mu_0 H_c \sim 0.2$ T. This is an insurmountable obstacle if the superconducting wires wound in coils should be used themselves to generate strong magnetic fields. In this sense, metallic alloys are way more appealing than their elemental counterparts for technological applications. The T_c value for the A15 intermetallic Nb_3Sn is around 18 K, while $T_c \simeq 23$ K for Nb_3Ge . Although liquid helium is still needed to exploit the superconducting dissipationless regime in these materials, the critical magnetic fields at zero temperature are typically several tens of Teslas. Thanks to their convenient fabrication and mechanical properties, metallic alloys are currently widespread in the high-power technological applications of superconductivity.

Different remarkable advancements have been achieved in the twenty-first century in the research on conventional superconductors by pursuing a common conceptual strategy, i.e., strengthening the phononic spectrum of materials – and superconductivity in turn – by lowering the nuclear masses of the constituting elements. This led to the observation of superconductivity with $T_c \simeq 39$ K in MgB_2 , as first reported by [Nagamatsu et al. \(2001\)](#) – see also [Buzea and Yamashita \(2001\)](#). At the same time, supported by the steady development of powerful computational tools allowing the ab-initio implementation of the BCS theory and motivated by an influential proposal published by [Ashcroft \(1968\)](#), researchers have been able to observe superconductivity with T_c values up to ~ 260 K in hydrogen-rich materials under high applied pressures. In particular, $T_c \simeq 203$ K has been reported for H_3S by [Drozdov et al. \(2015\)](#) quickly followed by the report of $T_c \sim 260$ K in LaH_{10} by [Somayazulu et al. \(2019\)](#) and [Drozdov et al. \(2019\)](#). The price for these remarkable fundamental achievements is the need to apply pressures up to hundreds of GPa which, at the moment of writing, makes these discoveries of limited interest for technological applications. An interesting account of high temperature superconductivity in hydrides has been published recently by [Flores-Livas et al. \(2020\)](#), but the field is currently witnessing an extremely fast development and, if confirmed, astonishing T_c values above ~ 550 K may be already at reach – see [Grockowiak et al. \(2020\)](#).

Superconductivity in Copper Oxides

The discovery of high temperature superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ by Johannes Georg Bednorz and Karl Alexander Müller dates back to 1986 and it acted as a complete paradigm shift in the research on superconductivity – see [Bednorz and Müller \(1986\)](#). Within few years of intense activity, the absolute record value for T_c in a superconductor at ambient pressure was raised from 23 K for Nb_3Ge to ~ 90 K for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ – see [Wu et al. \(1987\)](#) – and eventually to ~ 135 K for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$, as reported by [Schilling et al. \(1993\)](#). For the first time, the superconducting state emerged at temperatures above the boiling point of liquid nitrogen, with far-reaching implications for efficient technological applications. From a more conceptual point of view, this required to dismiss Matthias' empirical prescriptions completely, as copper oxides (or cuprates) are magnetic insulators with an anisotropic crystalline structure and, crucially, oxygen plays a role of major importance in determining their overall electronic properties.

Copper Oxides

The main structural unit characterizing all cuprate oxides is a two-dimensional CuO_2 plane, where Cu ions are arranged at the vertices of a square lattice and each Cu is octahedrally-coordinated with six O ions (see [Fig. 3](#)). Cu is in a nominal $2+$ valence state and, based on the electronic configuration $3d^9$, it carries one hole. In an octahedral crystal field, the system is subject to a marked Jahn-Teller distortion leading to an out-of-plane elongation of the octahedron and to a splitting of the Cu-derived e_g doublet in the lower $3d_{3z^2-r^2}$ and the upper $3d_{x^2-y^2}$ orbitals, in turn, the latter being occupied by the hole. Four O ions bridge the Cu ions along the lattice edges and, in this configuration, the electronic properties of each plane arise from the strong covalent σ bond between the $3d_{x^2-y^2}$ orbital from Cu and the $2p_x$ and $2p_y$ orbitals from O (see [Fig. 3B](#)). The most general structural model describing the crystalline structure of cuprates is a stacking of these CuO_2 layers. Blocks made up of a number N of CuO_2 planes are separated by spacing elements acting as charge reservoirs. The prototypal perovskite La_2CuO_4 belongs to single-layer ($N = 1$) materials, while $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Bi}_2\text{Sr}_2\text{Ba}_2\text{Cu}_3\text{O}_{10-\delta}$ are representative compositions for double-layer and triple-layer compounds, respectively. Proper chemical substitutions in the spacing layers can realize an effective charge doping of the CuO_2 planes, of either hole- or electron-type.

Based on the previous arguments, conventional single-electron band theory would predict a metallic ground state for the undoped “parent” compositions which, however, is not observed experimentally. In particular, a sizeable conductivity gap is measured which can be justified by considering the combined effect of the on-site $d-d$ Coulomb repulsion energy and the charge-transfer energy Δ_{CT} . In the specific case of cuprates, the relevant interaction is the latter and is associated with the different potential energy of Cu $3d_{x^2-y^2}$ and O $2p$ orbitals, as discussed in [Zaanen et al. \(1985\)](#) – as a result, the ground state is insulating and the system is dubbed “charge-transfer insulator” – see [Fig. 4](#). Accordingly, the holes are effectively localized on their original Cu ion

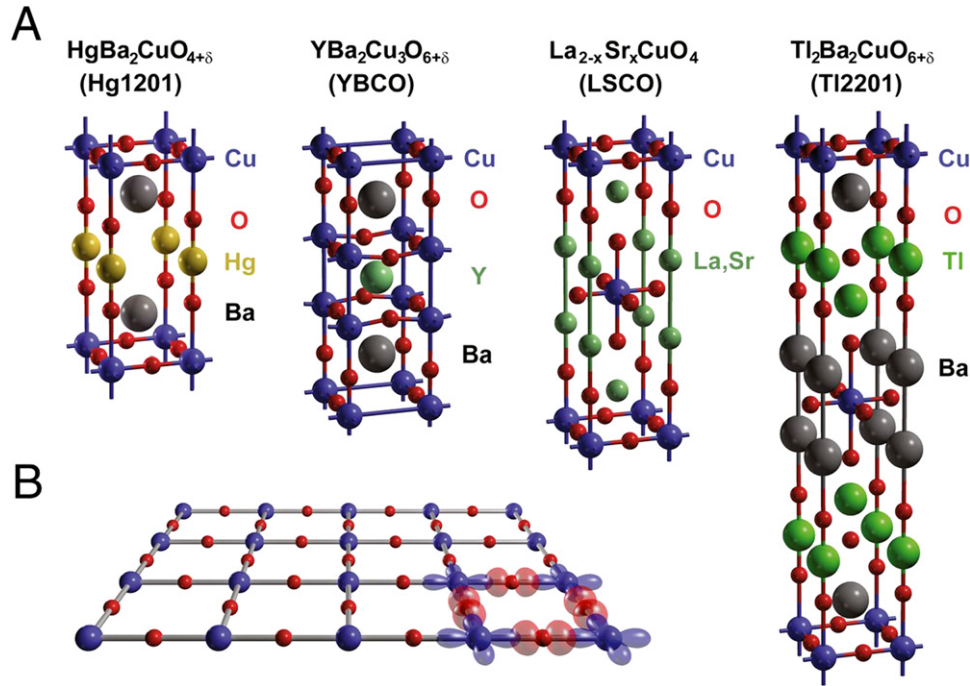


Fig. 3 Panel A displays the crystal structures of representative cuprate oxides. The CuO_2 plane is a common structural element to all families and it is shown in panel B, where the covalent σ bonds between the $3d_{x^2-y^2}$ orbitals from Cu and the $2p_x$ orbital from O are highlighted as well. The figure is reproduced from Barišić, N., Chan, M.K., Li, Y., *et al.*, 2013. Universal sheet resistance and revised phase diagram of the cuprate high-temperature superconductors. *Proceedings of the National Academy of Sciences* 110, 12235–12240.

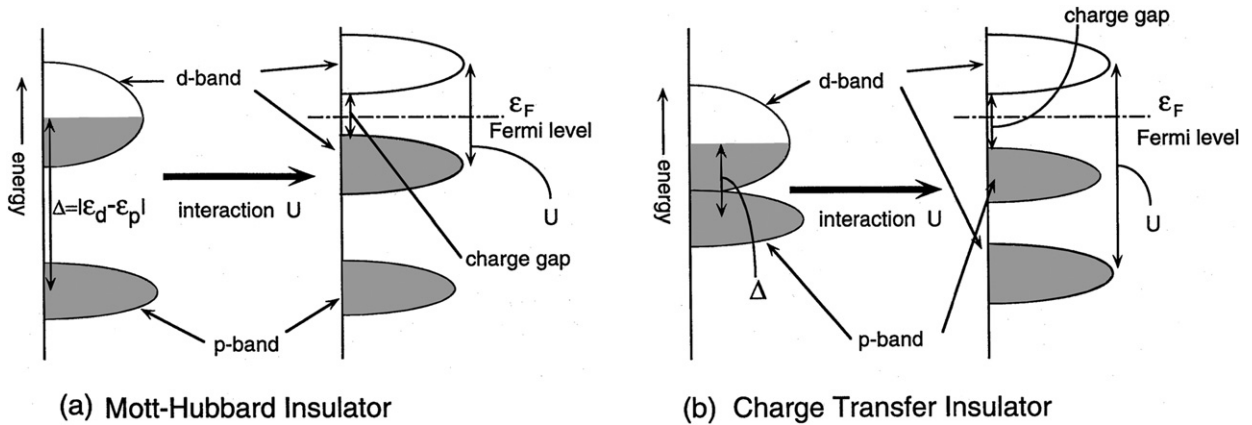


Fig. 4 Typical band structures characterizing Mott-Hubbard and charge-transfer insulators (left-hand and right-hand panels, respectively). The figure is adapted from Imada, M., Fujimori, A., Tokura, Y., 1998. Metal-insulator transitions. *Reviews of Modern Physics* 70, 1039–1263.

and are allowed to hop on adjacent sites only at a high energy cost. In agreement with the Pauli exclusion principle, these hopping processes are allowed only if the hole spins are antiparallel and this underlies the strong antiferromagnetic correlations which are observed in the ground state of the parent compounds.

These arguments can be made more quantitative by referring to the so-called Mott-Hubbard model, which is based on two essential competing energy scales – the energy gain obtained by delocalizing the electrons between different sites (t) and a repulsive term favouring the single site occupancy (U). The Mott-Hubbard hamiltonian is then written as

$$\mathcal{H}_{MH} = -t \sum_{i,j}^{n.n.} (c_{i\uparrow}^\dagger c_{j\uparrow} + c_{i\downarrow}^\dagger c_{j\downarrow} + h.c.) + U \sum_i (c_{i\uparrow}^\dagger c_{i\uparrow})(c_{i\downarrow}^\dagger c_{i\downarrow}) \quad (2)$$

where the indexes i and j run over the lattice sites and $n.n.$ restricts the first sum to nearest neighbors only. The fermion operators

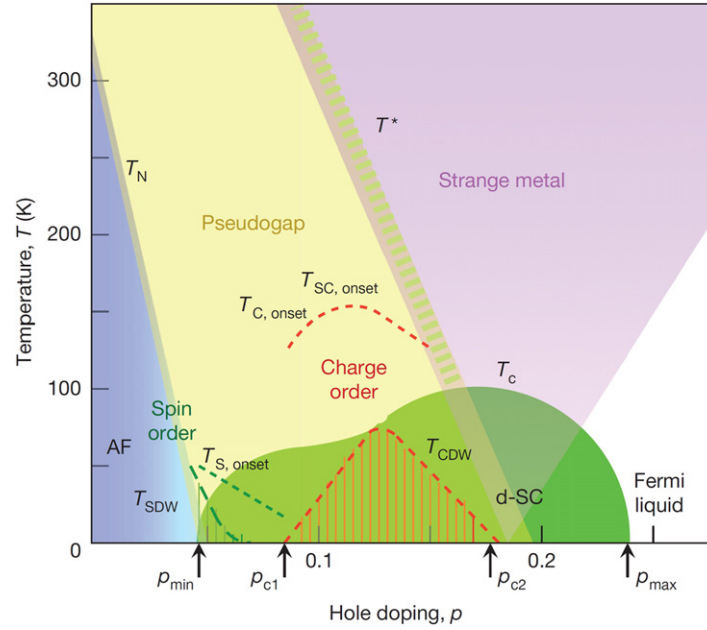


Fig. 5 Characteristic electronic phase diagram for cuprate oxides as a function of charge doping. The figure is reproduced from Keimer, B., Kivelson, S.A., Norman, M.R., Uchida, S., Zaanen, J., 2015. From quantum matter to high-temperature superconductivity in copper oxides. *Nature* 518, 179–186.

$c_{is}^\dagger$ and c_{is} respectively create and destroy a single electron at the site i with spin state s and $h.c.$ stands for hermitian-conjugated terms. Accordingly, the first term in the hamiltonian models spin-conserving hopping processes between adjacent sites while the second term quantifies the repulsive energy due to the on-site electron densities $n_{is} = c_{is}^\dagger c_{is}$. This hamiltonian interpolates between the scenarios describing conventional metals ($t \gg U$) and Mott insulators ($t \ll U$) and, as such, it is the starting point to describe the physics of metal-to-insulator transitions, as discussed by Imada *et al.* (1998). In the Mott-insulating limit ($t \ll U$), based on the so-called $t - J$ model – see Auerbach (1994) and Lee *et al.* (2006) – it can be shown that the second term of the hamiltonian in Eq. (2) can be mapped to a Heisenberg term $\sim (t^2/U) \sum_{ij} n_i n_j \mathbf{s}_i \cdot \mathbf{s}_j$ where the term between parentheses plays the role of an effective positive exchange energy favouring an antiferromagnetic arrangement. The transition temperatures to the long-ranged magnetic order for undoped cuprates are typically around several hundreds of Kelvin degrees, as in the case of La_2CuO_4 where $T_N \simeq 305$ K – see Carretta *et al.* (2011).

Unconventional Superconductivity

Naively, the discussion above implies that cuprate oxides are not expected to be a fertile ground for the development of superconductivity. Their ground state is strongly insulating and it hosts a robust antiferromagnetic phase – moreover, the strong characteristic charge-transfer energy $\Delta_{CT} \sim 1$ eV (corresponding to $\sim 10^{-19}$ J) leads to a high effective repulsive energy U among electrons which, in principle, can inhibit the generation of any bound Cooper pair. However, the remarkable experimental evidence is that the progressive increase of charge doping drives a complete suppression of the magnetic phase in favor of superconductivity (see the representative electronic phase diagram in Fig. 5). The critical temperature T_c is dependent on the doping fraction x in a non-monotonous fashion. In particular, T_c gradually increases upon increasing x , it takes a maximum value at the so-called optimal doping x_{opt} and then it is suppressed upon increasing x beyond x_{opt} . It is then customary to refer to the T_c vs x trend as the “superconducting dome”, while the superconducting regimes for $x < x_{opt}$ and $x > x_{opt}$ are dubbed “underdoped” and “overdoped”, respectively. Eventually, a conventional Fermi-liquid state is observed upon further increasing x beyond the overdoped regime. Naively, the progressive increase of x leads to a gradual decrease for the U/t ratio (see Eq. (2)) and to an insulator-to-metal transition favouring high temperature superconductivity when $U \sim t$. It is remarkable that the same phenomenology is observed both for hole and electron doping, even though in an asymmetric fashion, i.e., hole doping is much more effective than electron doping in the suppression of the magnetic ground state – see Maple (1990), Lee *et al.* (2006) and Armitage *et al.* (2010).

The superconducting state realized in cuprates is highly peculiar and, in many aspects, distinct from the phenomenology recalled above for conventional superconductors. The main discrepancy concerns the phononic mechanism behind the Cooper pairing which is, for cuprate oxides, of different and – at the time of writing – unknown origin. The characteristic energies of phononic modes in cuprate superconductors are indeed too low to justify T_c values higher than ~ 30 K and, accordingly, several alternative proposals have been put forward to model the microscopic pairing mechanism. In this sense, the observation that the superconducting dome is located in close proximity to the suppression of the magnetic state is often considered as a particularly relevant experimental

evidence, together with the persistence of clear signatures of spin dynamics inside the superconducting phase – as detected by NMR and neutron scattering. These observations underlie the spin fluctuations exchange model for the pairing mechanism, in analogy with the theoretical models underlying the pairing in the superfluid phase of ^3He – see Leggett (1975) and Moriya and Ueda (2000). This theory is particularly appealing in view of a seemingly universal behavior observed for other classes of high temperature superconductors such as iron-based pnictides and chalcogenides, heavy fermions and actinides – see Scalapino (2012) and Chubukov (2012) for more details.

Another important qualitative difference between the superconducting state in metallic materials and in copper oxides is the isotropy of the energy gap Δ in the momentum space. Superconductivity in elemental metals is a fully-gapped electronic state, i.e., the gap value is isotropic, as reflected in the low-temperature exponential behavior for, e.g., the specific heat and the spin-lattice relaxation rate in NMR experiments. However, Δ shows a marked dependence on the wave vector $\mathbf{k}$ in cuprates and it even changes sign, implying the existence of nodal points where $\Delta = 0$. As a result, the dependence of several experimental quantities of interest on temperature is no longer exponential but it rather follows a power-law. Also, the marked structural anisotropy of cuprates typically results in highly anisotropic superconducting properties in real space as well, with, e.g., a marked dependence of the penetration depth λ_L on the sample orientation with respect to the external magnetic field.

The stabilization of a superconducting ground state at relatively high temperatures makes qualitatively novel phenomena emerge which would be otherwise not observable in conventional superconductors. This is particularly the case for the thermal fluctuations of the superconducting order parameter above the critical temperature T_c . The mean-field character of the superconducting transition in metallic superconductors, together with the low characteristic T_c value, makes indeed the extension of the critical regime unmeasurably small. However, as recently reviewed by Varlamov *et al.* (2018), the higher thermal energies together with the smaller coherence lengths (and smaller spatial dimensions of the Cooper pairs) contribute to enhance the fluctuative contribution above T_c to several experimental quantities of interest, such as the heat capacity, the conductivity, the Nernst-Ettingshausen signal and the magnetization. At the same time, the high thermal energies at play in cuprate oxides lead to interesting consequences for the vortices in the Shubnikov state. Vortices are characterized by a mutual repulsive interaction and under ideal conditions they generate a – typically triangular – long-range ordered lattice, where the density of vortices can be tuned by the amplitude of the applied magnetic field. Non-idealities arise from quenched disorder and structural defects which act as “pinning” centers, anchoring vortices and thereby distorting the geometrical properties of the lattice. High temperatures can favor thermally-activated depinning processes which cause a motion of vortices and result in a major energy dissipation even within the superconducting phase. A similar effect is caused by electrical currents which, as a general result, exert a transversal hydrodynamic-like force on the vortices, thus favouring their motion. As a result of this complicated interplay of different competing interactions, thoroughly reviewed by Blatter *et al.* (1994), the Shubnikov phase is typically divided in solid and liquid phases for the vortices (see Fig. 6). A variety of different subphases – both static and dynamic – can be realized for the vortices, making the problem particularly interesting from a fundamental point of view. At the same time, the problem has far reaching implications from a more technological application-oriented perspective. In other words, defects should be properly engineered to guarantee a strong pinning efficiency and stability of the vortices in order to exploit the dissipationless transport properties of superconductors – see MacManus-Driscoll and Wimbush (2021).

Phase Diagram

In the previous section, we mentioned that the increase of the charge doping fraction x – of either hole or electron character – progressively suppresses the antiferromagnetic charge-transfer-insulating ground state in favor of high temperature superconductivity and, eventually, of a conventional Fermi-liquid metallic state (see Fig. 5). However, interesting and unexpected physical properties are found also by studying the high-temperature electronic phases from which the low-temperature magnetic and superconducting ground states are derived. This journey through the T - x electronic phase diagram of cuprate will reveal the impressive complexity of these materials which, at the time of writing, is still not fully understood – see Keimer *et al.* (2015).

A wide section of the phase diagram is occupied by the so-called pseudogap state, observed below a characteristic temperature T^* which is suppressed by the progressive increase of the charge doping, even though at a slower rate if compared to T_N . In the T - x electronic phase diagram, the pseudogap state “covers” the antiferromagnetic ground state and the superconducting dome in the underdoped regime. Experimentally, the pseudogap is characterized by a sharp reduction of the density of states at the Fermi energy, akin to the generation of a gap in the excitation spectrum, but in the absence of any symmetry-breaking phase transition. The development of such gap is reflected in several experimental quantities, as reviewed by Timusk and Statt (1999) – however, there is no consensus about its nature. A proposed scenario suggests that the electrons start pairing up for $T < T^*$ even though the achievement of long-range phase coherence among the different pairs is then achieved only below T_c . Eventually, close to the condition of optimal charge doping, the normal metallic phase evidences highly unusual properties such as a linear dependence of the resistivity on temperature. This state is dubbed “strange metal” and recent proposals rely on models belonging to the realm of string theory for its description – see Sachdev (2010, 2012) and Sachdev (2015).

It is known that the competition of different energy scales in transition-metal oxides (hopping integral and on-site repulsion, as seen above, but also exchange interaction and vibrational energies) leads to the emergence of spatially-inhomogeneous ground states – see Dagotto (2005) for a thorough review on the subject. Cuprates are no exception to this framework. In particular, the typical electronic phase diagram reported in Fig. 5 evidences the development of a spatial modulation of the charge density, also

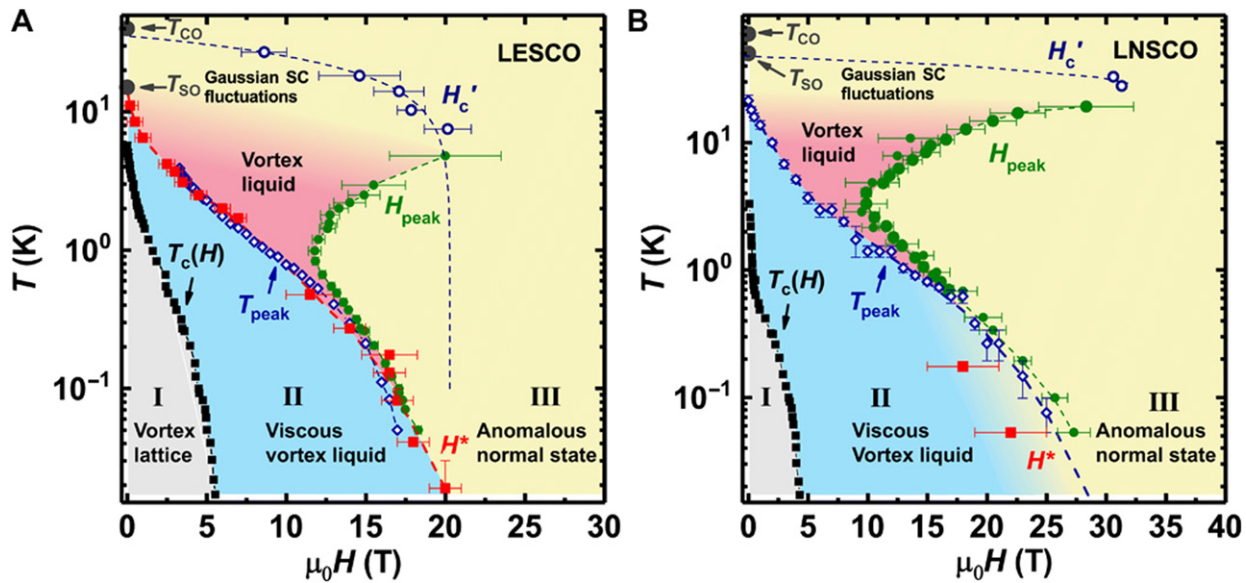


Fig. 6 Representative H - T phase diagram for the vortex lattice in $\text{La}_{1.7}\text{Eu}_{0.2}\text{Sr}_{0.1}\text{CuO}_4$ (LESCO, panel A) and $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$ (LNSCO, panel B). The figure is reproduced from Shi, Z., Baity, P.G., Sasagawa, T., Popović, D., 2020. Vortex phase diagram and the normal state of cuprates with charge and spin orders. *Science Advances* 6, (eaay8946-1 – eaay8946-9).

known as charge density wave (CDW), which is ubiquitous in cuprate materials – see Grüner 1988; Tranquada *et al.*, 1995; Wu *et al.*, 2011; Ghiringhelli *et al.*, 2012; Comin *et al.*, 2014; da Silva Neto *et al.*, 2014; Arpaia and Ghiringhelli (2021). The CDW is static for certain hole doping levels and it gives rise to a modulation which can be commensurate with the lattice and to the appearance of hole rich and hole poor stripes predicted within different theoretical approaches, as reported in Zaanen and Gunnarsson (1989); Emery *et al.* (1990) and Castellani *et al.* (1995). Although the CDW order parameter is expected to be larger at low hole doping levels, the development of resonant X-ray scattering techniques has clarified that this phase extends into the overdoped regime, at doping levels well beyond the one leading to the maximum T_c , where the electronic correlations are weaker – see Miao *et al.* (2021). The role of the CDW excitations, favouring or competing with the pairing mechanism, is still subject of debate – see Caprara *et al.* (2020). It should be mentioned that recent theoretical modeling relates the observation of CDW order in cuprates to a putative “pair density wave” (PDW) state where the superconducting order parameter itself is spatially modulated, leading to a complex scenario with an effective spatial intertwining of spin, superconducting and charge degrees of freedom – see Berg *et al.*, 2009; Fradkin *et al.* (2015) and Agterberg *et al.* (2020).

Superconductivity in other Oxides

The results reviewed above for cuprates motivated an extended hunt for superconductivity in other families of oxides over the last decades, aiming at a similar phenomenology and possibly at higher T_c values.

Superconductivity was reported in a Pb- and Bi-based oxide already well before the pioneering work of Bednorz and Müller. In particular, Sleight *et al.* (1975) studied $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ and found evidences of bulk superconductivity with T_c values up to ~ 13 K – see also Baumert (1995) and Sleight (2015). However, it was only soon after the discovery of high temperature superconductivity in cuprates that Mattheiss *et al.* (1988) and Cava *et al.* (1988) reported remarkably high T_c values around 30 K for the charge-doped bismuth oxide $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$. In spite of several experimental evidences of a marked oxygen isotope effect – see Hinks *et al.*, (1988) and Batlogg *et al.* (1988) – numerical approaches based on density-functional theory have shown that the electron-phonon coupling in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is too small to justify transition temperatures as high as 30 K – see, for example, Meregalli and Savrasov (1998). In fact, more recent work by Yin *et al.* (2013) pointed to the inadequacy of density-functional theory in the local-density approximation in the presence of long-range Coulombic interactions. On these bases, Wen *et al.* (2018) demonstrated through angle-resolved photoemission spectroscopy that $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is “a benchmark BCS superconductor”. Still, it is remarkable that the development of a CDW phase is shared between cuprates and bismuthates – see Uchida *et al.* (1987). The charge-density wave extends over a wide range of the phase diagram in both K-doped and Pb-doped compounds – see Nicoletti *et al.* (2017). The same phenomenology was evidenced very recently in the closely related family of antimony oxides $\text{Ba}_{1-x}\text{K}_x\text{SbO}_3$ – see Kim *et al.* (2021). In these latter compounds, superconductivity emerges with a T_c approaching 15 K as the CDW order is suppressed via potassium substitution, suggesting a strong competition between the two ground states.

Finally, the proximity of nickel to copper on the periodic table and the identical $3d^9$ electronic configuration realized for both Cu^{2+} and Ni^{2+} ions make nickel oxides, or nickelates, attractive candidates to reproduce the electronic phases observed in cuprates

– see Anisimov *et al.* (1999) and Hansmann *et al.* (2009). In fact, Lee and Pickett (2004) stressed major qualitative differences in the electronic structures of undoped nickelates and cuprates resulting in a characteristic metallic state for the former opposite to the strongly insulating properties of the latter – see also Botana and Norman (2020). The difficulty in synthesizing compounds with nickel in a $1+$ oxidation state prevented experimental steps forward until the recent report of superconductivity in hole-doped NdNiO_2 by Li *et al.* (2019) with $T_c \sim 10$ K, later confirmed by Li *et al.* (2020) and Zeng *et al.* (2020) as a function of the hole doping amount – see also the commentary by Pickett (2021). At the moment of writing (2021) the field is in rapid expansion and, remarkably, superconductivity is observed only in thin film samples and not in bulk compounds – see Wang *et al.* (2020).

Closing Remarks

In this article, we described the rich and complex physics of the electronic phase diagram of copper-based oxides. The focus has been on the development of high temperature superconductivity with additional important references to the Mott-insulating antiferromagnetic state of undoped materials and to spatially inhomogeneous phases such as the charge-density wave. We highlighted the main qualitative differences of cuprate superconductors and other superconducting materials such as elemental metals, bismuthates and nickelates.

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Conductometric Gas Sensors

Gayan WC Kumarage and Elisabetta Comini, Sensor Laboratory, Department of Information Engineering, University of Brescia, Brescia, Italy

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Abstract

The main focus of this article is to describe the basic but important perspectives of gas sensors, especially, conductometry metal oxides (MOXs). Fundamental functions, drawbacks, and factors influencing the sensor's performances are explained. Furthermore, the enrollment of nanostructured materials and novel technology to enhance the sensing performance is also discussed. MOXs gas sensing mechanism is described to provide guidelines and knowledge to improve the sensing performances. Moreover other gas sensing devices are briefly discussed to have a clear overall picture of gas sensors.

Introduction

One of the excellent sensors in nature, the human nose, has the tremendous ability to smell one trillion odors from its 400 types of scent receptors. However, it is still not able to monitor and quantify air-polluting chemical stimulus or variations and its concentration accurately to avoid physical problems such as headache, skin/eye irradiation, coughing, breathing difficulties, fainting, and even superficial death. So, nearly 7 million (~8%) of the global total deaths in 2012 and 12% in 2019 have been reported ([Stateofglobalair.org](https://www.stateofglobalair.org), 2022) due to air pollution. The main environmental pollutants in the atmosphere, such as carbon dioxide (CO₂), carbon monoxide (CO), sulfurous oxides (SO_x), nitrous oxides (NO_x), hydrocarbons, and volatile organic compounds (VOCs) ([Manisalidis et al., 2020](#)) brings drastic issues on environment and living beings. These pollutants are generated from various sources and activities, belong to two major groups. One is man-made or anthropogenic sources (transportation, power plants) and the second is natural sources (lightning, soils, fires, and volcanoes) ([Olivier et al., 1998](#)). Indeed, these primary pollutants are capable of transforming into more hazardous secondary species such as ozone (O₃) and other various compound and oxides based on sulfur and nitrogen ([Hopke et al., 2020](#)). Credit to mother nature these primarily and secondary pollutants are removed and underground by dry or wet deposition mechanisms. Unfortunately, a considerable amount of these pollutants stays in the atmosphere, bringing adverse effects not only to human health but also to the environment and ecosystems. Hence, demand for high-performance sensors that are capable of detecting environmental pollutants, such as volatile/semi-volatile organic compounds (VOCs/SVOCs), harmful gases, particulars, and chemical compounds is increasing daily. Besides, these sensors should fulfill several important requirements such as high sensitivity, selectivity, stability, reliability, low power consumption, durability, cheapness, and ease to use to be regarded as the more meaningful sensors for real applications. Achieving these goals, many sensors have successfully entered the human habitual routine to measure many parameters of the environment as well as of the human body, in which GAS SENSORS are among the most convenient in detecting numerous amounts of toxic gases and VOCs. A gas sensor is a device that detects the presence and eventually the concentration of an analyte gas in a nearby environment and transforms chemical information into an analytically useful signal.

Usually, a gas sensor device ([Fig. 1](#)) is built with three major parts; (1) a system for delivery of the gas which carries out its sampling, filtering, and preconditioning; (2) a system for detection of the analyte gas which consisting of the sensing element that converts the chemical interaction into an electrical signal (or capacitance, absorption, etc.). A detection system can be prepared in either planner or tubular manner as shown in the inset of [Fig. 1](#). The third part is the computing system which can evaluate data and convert them into an interpretable format ([Röck et al., 2008](#)). The most important part to be discussed in this article is the detection system, which concerns sensing elements/active materials of the device. Usually, semiconducting metal oxide (MOX), polymers, carbon nanotubes (CNT) materials are used as the active materials. Once, the analyte gas interacts with the sensing element it modifies a signal, indeed, the concentration and/or type of the analyte gas cause a variation in this output signal. Usually, the output signal is an electrical, optical, calorimetric, or acoustic parameter that can be integrated into different types of gas sensors as shown in [Fig. 2](#). However, each method has its own pros and cons as well as unique applications ([Table 1](#)). Concerning specific advantages such as cheap, mass production, reliable integration capabilities, and miniaturization over other categories of gas sensors, semiconducting (metal oxide) conductometry sensors are among the best choice for future internet of things (IOT) applications.

Metal Oxide (MOX) Gas Sensors

The first idea of employing semiconductors to detect chemical species in the environment begins in the early 1950s. This innovative idea was based on the observation of a change in electrical resistance of Ge when exposed to different atmospheric conditions ([Brattain and Bardeen, 1953](#)). Consequently, the first chemiresistive MOXs gas sensor was introduced in the 1960s based on ZnO thin film as a sensing element for sensing propane at an operating temperature of 485 °C ([Seiyama et al., 1962](#)). However, it took one decade to fabricate the first patented chemiresistive MOXs gas sensor device for real applications in which the sensing element was tin dioxide (SnO₂) ([Taguchi, 1971](#)). This device was based on SnO₂ porous thick film. Meanwhile, Taguchi

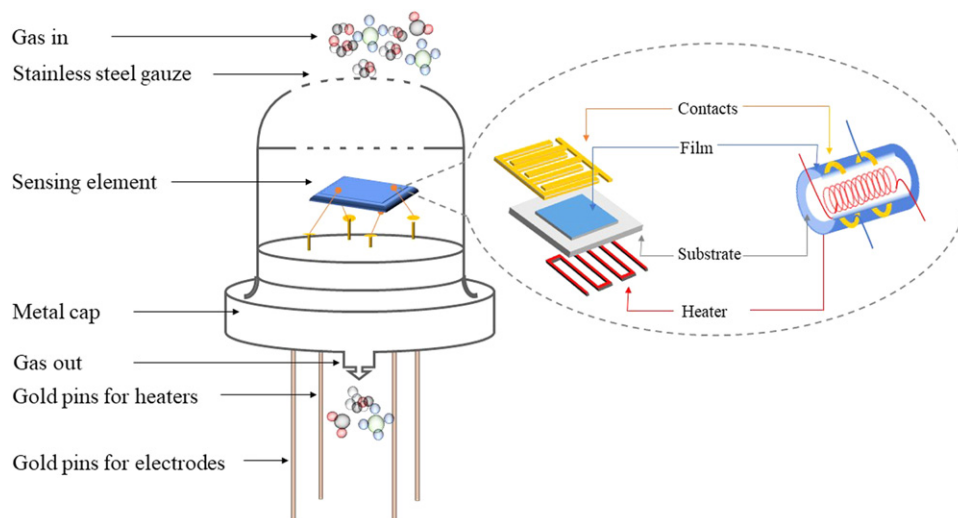


Fig. 1 The general structure of a gas sensor. Planar and tubular configuration of sensing element are reprinted with the permission of Kumarage and Comini. Reproduced from Kumarage, G., Comini, E., 2021. Low-dimensional nanostructures based on cobalt oxide (Co_3O_4) in chemical-gas sensing. *Chemosensors* 9 (8), 197.

enhanced the sensitivity of the device based on the pinner invention by Shaver in 1967 (Shaver, 1967), by decorating SnO_2 with Pd catalyst before the commercialization by Figaro Inc. for alerting possible domestic fire accidents. Afterward, the field of gas sensors underwent a tremendous expansion in researching high-performance gas sensors to achieve high sensitivity, selectivity, faster response, low power consumption, high device reliability, and low production costs.

Metal oxides like SnO_2 , WO_3 , TiO_2 , WO_3 , Fe_2O_3 , ZnO , and In_2O_3 (Fig. 3) have been extensively studied in the form of their pristine thick films to highly technological nanostructures ascribed to pinner invention by Yamazoe in 1991 which shows the reducibility of crystallite size (Yamazoe, 1991). Accordingly, the synthesis of low dimensional MOXs nanostructures for conductometry gas sensors has been expanding all over the last years and became the most active research area within the nanoscience community (Xia *et al.*, 2003; Comini, 2020). Today, the field of conductometric gas sensors is dominated by nanotechnology to mitigate several challenges such as poor selectivity, slow response/recovery times, sensitivity, and high operating temperatures (Cho *et al.*, 2019).

General Performances of Metal Oxide Gas Sensors

The main characteristics of gas sensors are response, selectivity, response time, recovery time, stability, gas detection limit, and operating temperature. The response may be defined as the ratio of the resistance (or conductance) of the sensing material expose to analyte gas (R_g) vs air (R_a) depending on which of the two is increasing. Selectivity is the capability of detecting the target analyte in a mixture of gases. Stability is the capability to maintain constant functional properties (electrical resistance) over time. Response time determines the time to accomplish 90% of the final resistance of the sensor when interacting with the gas. A typical dynamic response curve of the MOX sensor is shown in Fig. 4(a). Although, recovery time is calculated as the time interval required to get back to 90% of the resistance value in the air before the gas introduction as the airflow is restored. The sensitivity is defined as the gradient of the sensor's response - concentration Fig. 4(b). Consequently, the minimum value of target gases' volume concentration (detection limit) can be extracted from this plot, in which obviously, the lower the value, the better the sensing performances of the gas sensors. Finally, the working temperature is the temperature of the sensing element when sensors operate (Kumarage and Comini, 2021).

Sensing Mechanism

The gas sensing mechanism of the MOXs sensors can be divided in two major functions called receptor and transducer functions. The receptor function concerns the interaction between the target gas and the solid interface, which alters the electronic properties at the semiconductor surface. The transducer function involves transducing the surface phenomenon into a readable signal, such as the electrical resistance change in the sensors for conductometric sensors (Dey, 2018). Furthermore, two interaction models, "ionosorption" and "oxygen vacancy" are involved in the receptor function. The oxygen vacancy model describes the response in MOXs due to the subsequent oxidation or reduction of the MOXs surface when interacting with a reacting gas species. Meanwhile, the ionosorption model describes the chemisorbed oxygen on the MOXs surface which is known as the main active species that induces a response (Gurlo and Riedel, 2007). Usually, gas sensors are used under normal atmospheric conditions (in the presence of air) where the oxygen chemisorption mechanism is dominant. Also, humidity possesses a significant role in the sensing mechanism.

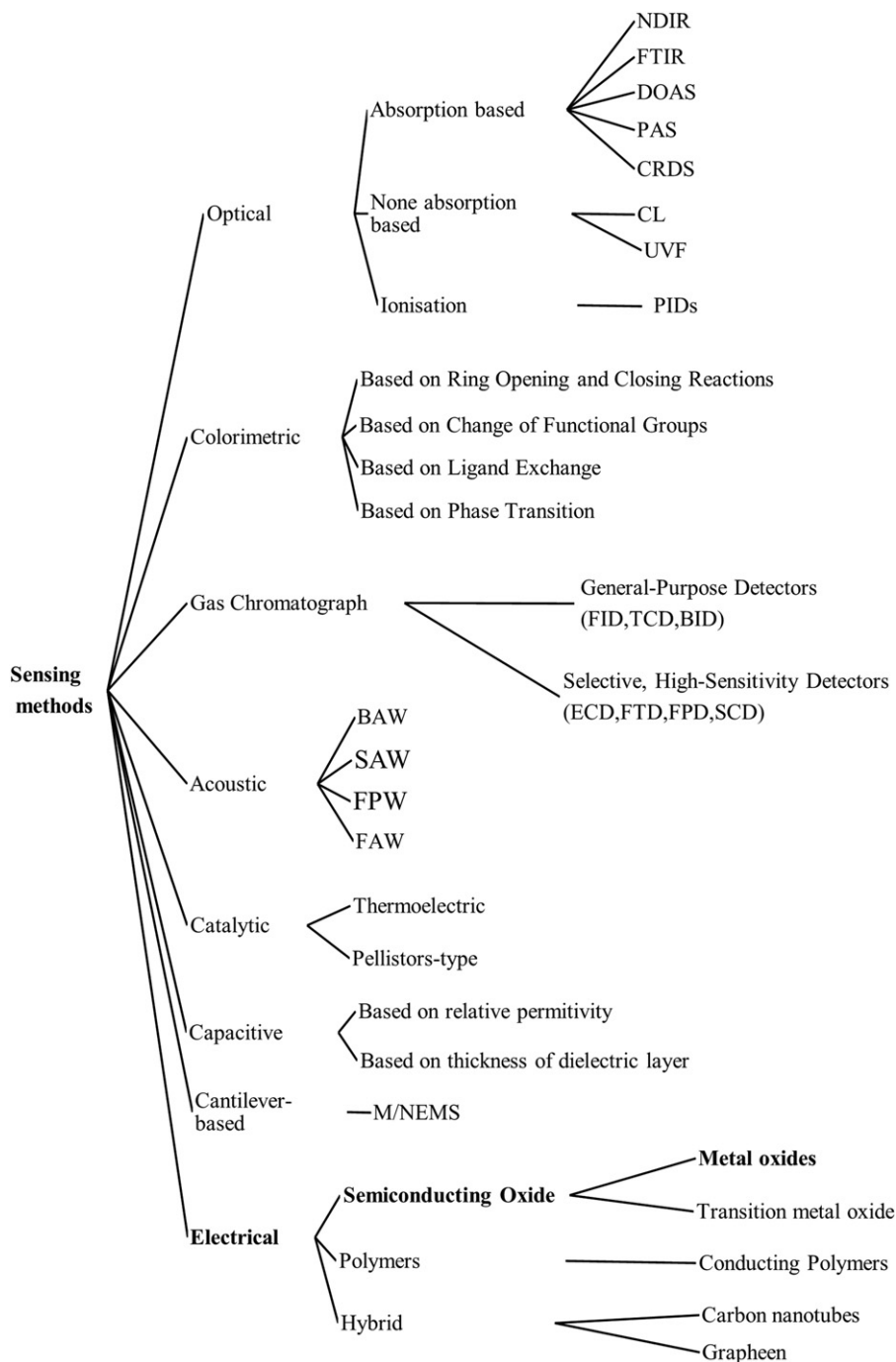


Fig. 2 General gas sensing methods and types of gas sensors.

Atmospheric oxygen

Atmospheric oxygen molecules play a significant role in conductance hence the sensing mechanism of the MOXs. The relationship between electrical conductivity and oxygen partial pressure of the MOXs sensor is shown in eq. (1) (Dey, 2018). Once, oxygen is chemisorbed, they are absorbed onto the MOXs surface. Accordingly, charge carriers (electron in n-type and holes in p-type MOXs) are extracted from the near-surface region up to a certain depth of the MOXs. This process forms oxygen species; molecular O_2^- , atomic O^- , and O^{2-} at the temperature $< 150^\circ C$, $150-400^\circ C$, and $> 400^\circ C$ respectively, as shown in the eqs. (2) – (4), on the MOX surface (Kumarage and Comini, 2021). Accordingly, an electron depletion region in an n-type (hole accumulating layer in p-type) will be formed. The formed electron depleted layer (or hole accumulating layer) acts as a potential barrier at the surface with a significant width and height. Thus, it would be interesting to explain briefly the changes.

Table 1 Basic gas sensing methods, advantages, disadvantage, and their application

<i>Methods</i>	<i>Advantages</i>	<i>Disadvantages</i>	<i>Application fields</i>
Electrical	(a) Low cost (b) Fast response time (c) High sensitivity (d) Low weight (e) Wide range of target gases	(a) Sensitive to environmental factors such as humidity (b) Energy consumption	(a) Industrial applications (b) Indoor air monitoring (c) Storage place of synthetic products such as paints, wax, or fuels
Optical	(a) High sensitivity, selectivity, and stability (b) Long lifetime (c) Insensitive to environmental change	(a) Difficulty in miniaturization (b) High cost	(a) Remote air quality monitoring (b) Gas leak detection systems with high accuracy and safety (c) High-end market applications
Infrared	(a) Highly selective and offer a wide range of sensitivities (b) The detector does not directly contact the gas (c) Corrosion resistance (d) Least amount of maintenance or replacement (e) Reliable design	(a) Perform poorly in extreme environments; high humidity, fog (b) Failure to detect hydrogen (c) Do not work well when multiple hydrocarbon-based gases	(a) Toxic and combustible gas monitoring (b) Industries, including the petrochemical industry
Calorimetric	(a) Stable at ambient temperature (b) Low limit of detection (c) Adequate sensitivity (d) Low power consumption	(a) Risk of catalyst poisoning and Explosion (b) Intrinsic deficiencies in selectivity	(a) Most combustible gases under industrial environment (b) Petrochemical plants (c) Mine tunnels (d) Kitchens
Gas Chromatograph	(a) Excellent separation Performance (b) High sensitivity and selectivity	(a) High cost (b) Difficulty in miniaturization for portable applications	Typical laboratory analysis
Catalytic	(a) Excellent Accuracy and reproducibility (b) Fast response (c) Low power consumption (d) Humidity independent response	(a) Catalytic poisoning (b) Sensor drift (c) Calibration	(a) Coal mines (b) Industrial sectors (c) Drunk driving detection
Acoustic	(a) Long lifetime (b) Avoiding secondary pollution (c) Detect nerve and blister agents	(a) Low sensitivity (b) Sensitive to environmental change (c) Difficulty in handling during the fabrication process	(a) Components of Wireless Sensor Networks (b) Electronic nose (c) Food quality testing
Cantilever	(a) Higher sensitivity (b) Fast response time (c) Low cost (d) Array format (e) Small overall dimensions	(a) Long-term stability (b) Poor performance in a viscous medium	Typical laboratory analysis such as health care, energy, security, artificial nose setup

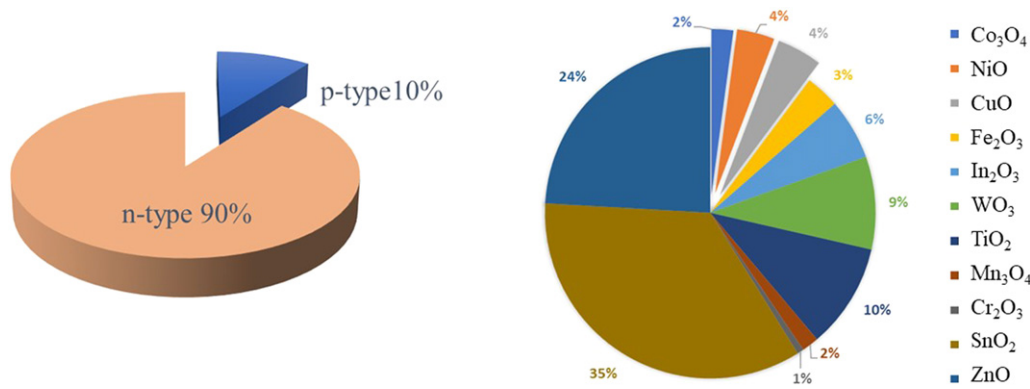


Fig. 3 Employment of metal oxide in the conductometry gas sensing.

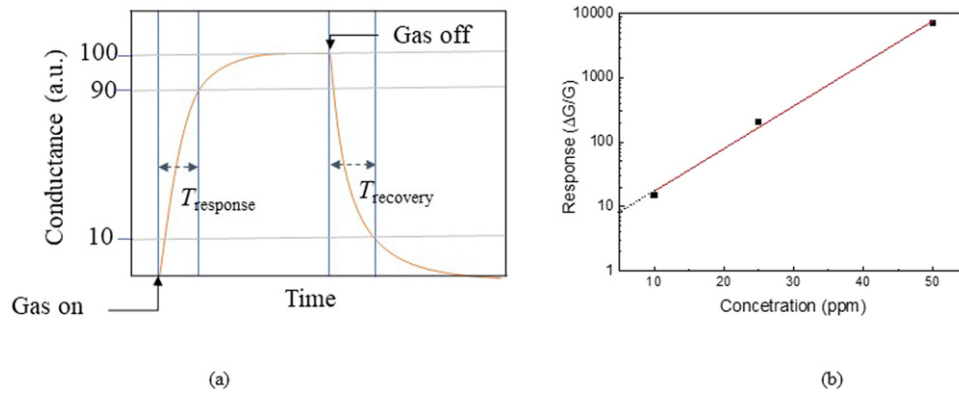


Fig. 4 The typical dynamic response curve of (a) an n-type MOX interacting with reducing gas; (b) power fitting of response vs gas concentration of a gas sensor.

$$\sigma = A \exp\left(\frac{-E_A}{kT}\right) P_0^{1/N} \quad (1)$$

σ - electrical conductivity

A - constant

E_A - activation energy

k - equilibrium constant

T - temperature

N - a constant depends on the bulk defects



The conductance of MOXs can be explained by the core-shell model. For instance, the outer shell of the grain is “insulating” because of the ionosorption of oxygen species, electron depletion (or hole accumulation) layer, as shown in Fig. 5(a-d). In which adsorbed oxygen molecules trap electrons from the conduction band of n-type (or valance band of p-type) MOXs and form pre-chemisorbed oxygen ions (O_2^-) on the surface at room temperature (Barsan and Weimar, 2001). Consequently, energy bands bend upward near the surface of n-type (or downward in p-type) MOXs (Fig. 5(e-h)) in comparison with the flat band situation before any surface reaction. This process hinders the electrical conductance in n-type MOXs. In contrast, resulting in an increment in conductance in p-type MOXs.

The formed potential barrier can be expressed as a function of distance with several estimations using the Poisson relations as shown in eq. (5). Usually, space charge density is equal to the net charge density in the depletion region, as in eq. (6). Meanwhile, the width of the depletion region is estimated using Debye length (L_D) as shown in eq. (7) (Yamazoe and Shimanoe, 2008). Accordingly, when material dimensions (grain size, D) are equal or shorter than the Debye length the entire structure is depleted (or accumulated) by adsorbed oxygen resulting highly resistive layer Fig. 6(a-c). Once, a reducing gas interacts, electrons are provided to the depletion layer resulting in a tremendous increment in the conductance of n-type MOXs, which is converse for p-type MOXs as shown in Fig. 6(d-e). A detailed explanation of the effect of grain sizes is described in section latter.

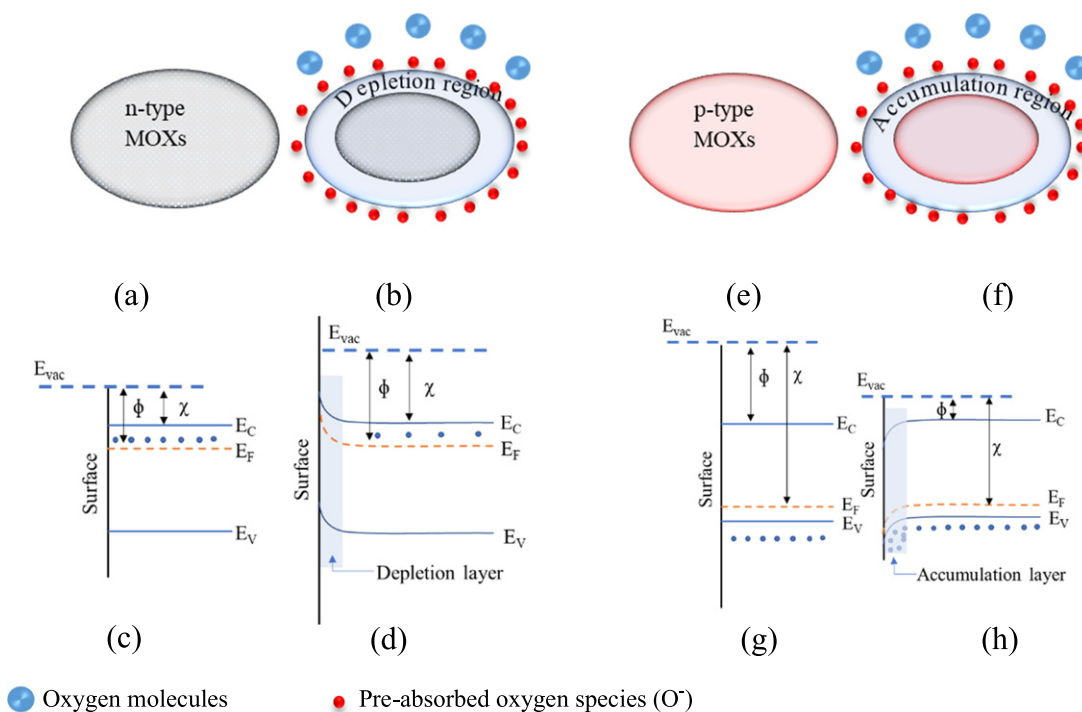


Fig. 5 Schematic at the near-surface when interacting with oxygen: (a)-(d) n-type; (e)-(h) p-type MOXs.

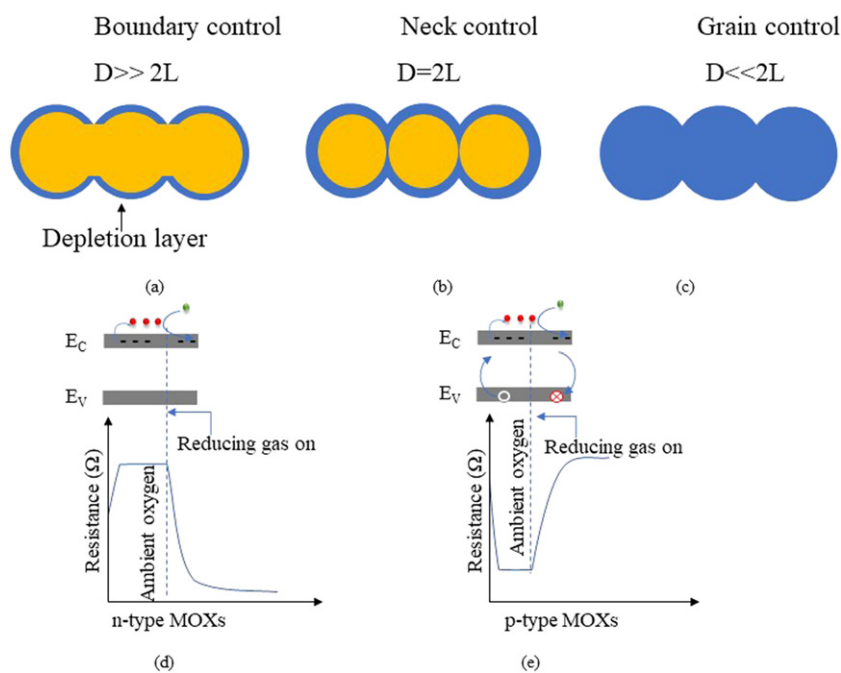


Fig. 6 Schematic show the effect of grain size (D) on the response of the sensor, (a) $D > 2\lambda_D$; (b) $D \geq 2\lambda_D$; (c) $D < 2\lambda_D$; resistance change when reducing gas interacts with (d) n-type; (e) p-type MOXs.

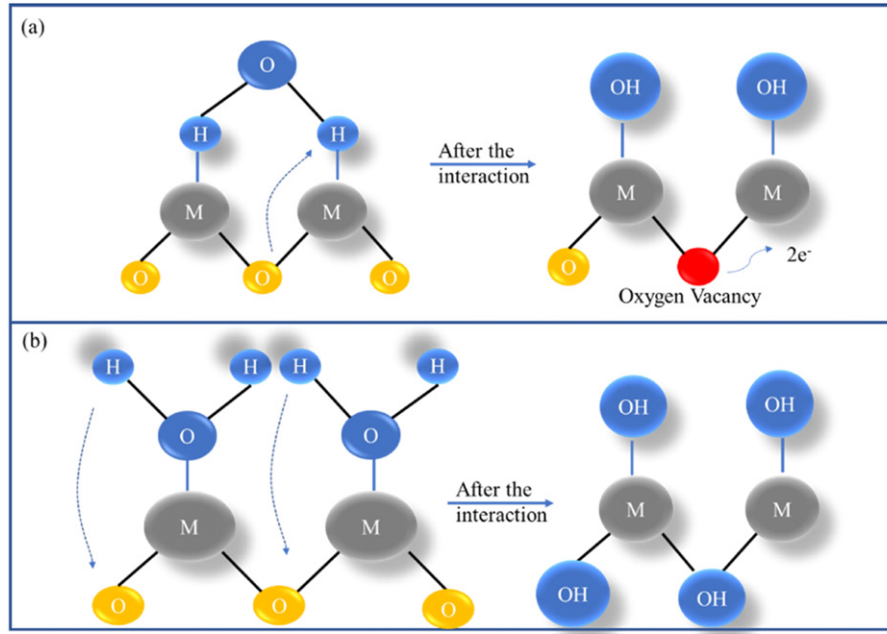


Fig. 7 Mechanisms of humidity adsorption on the surface of metal oxide; (a) low humidity and (b) high humidity.

$$\frac{d^2V(x)}{dx^2} = \frac{\rho(x)}{\varepsilon} \quad (5)$$

$V(x)$ - estimated potential

ε - dielectric constant

$\rho(x)$ - space charge density

$$\rho(x) = q[N_d^+(x) - n(x)] \quad (6)$$

q -charge of the electron

$N_d^+(x)$ -density of ionized donors

$n(x)$ density of electron at a given depth (x)

$$L_D = \sqrt{\frac{\varepsilon k_B T}{q^2 N_d}} \quad (7)$$

ε - dielectric constant

k_B - Boltzmann's constant

T - absolute temperature

N_d - donor density

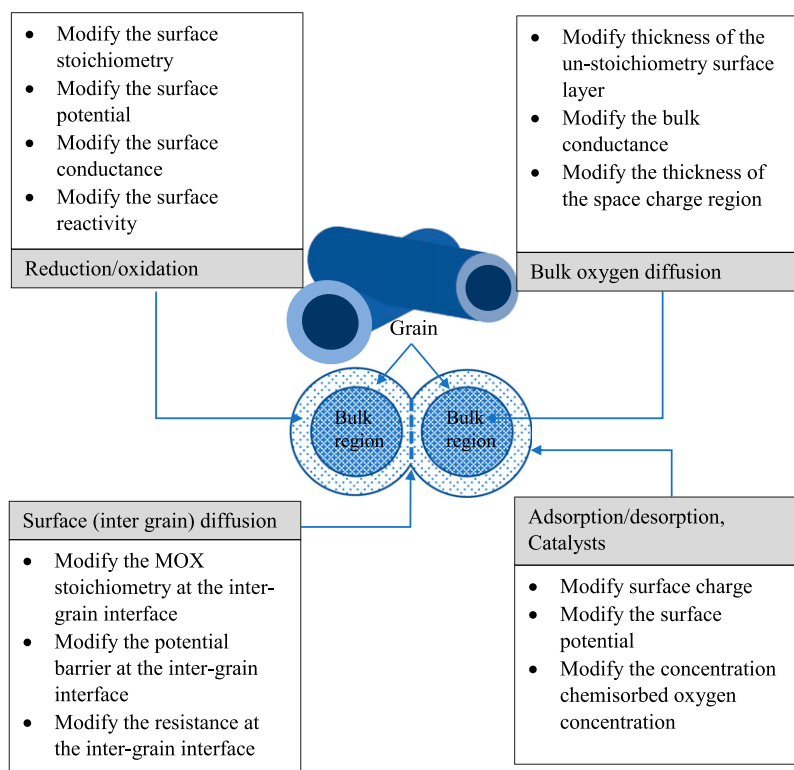
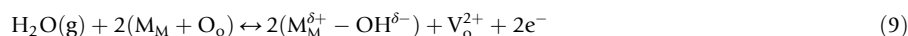
Atmospheric humidity

Water (H_2O) vapor molecules in the atmosphere are also significantly changing the baseline resistivity as well as the sensitivity of the MOXs sensors. Water molecules are absorbed onto the MOXs and modulate MOXs electrical properties. First, they may reduce the number of absorbed oxygen species. On the other hand, they may alter the baseline resistivity due to the chemisorption process. Hydroxyl groups (OH^-) are formed on the surface of the MOXs resulting in sensing performances change (Saruhan *et al.*, 2021). In detail, water molecules are absorbed onto the MOX surface, as shown in Eq. (8). Subsequently, the ratio of H_2O to the active site governs the absorption mechanism where chemisorption is dominant in low humidity and physisorption is dominant in a high humidity environment. In low humidity conditions, H_2O molecule interacts with two metal oxide resulting in two M-OH dipoles (M stands for metal) and two free electrons from each oxygen vacancy (V_o^{2+}) in lattice during the formation of M-OH bond, as shown in Fig. 7(a) and Eq. (9). In high humidity conditions each H_2O molecule will interact with two metal oxides as shown in Fig. 7(b) and Eq. (10). So, dissociated hydroxyl ions are bonded with each metal site. Meanwhile, hydrogen ion diffuses into the lattice to bind with lattice oxygen, thus forming two hydroxyl bonds per metal site. The adsorbed OH^- group acts as a donor due to lower electron affinity and ionization whereas, the oxygen vacancies will act as the acceptors (Traversa, 1995). Accordingly, humidity has adverse effects on the sensor's performance lowering the response, slowing it down, and increasing the recovery time.



Table 2 General process affecting to MOXs gas sensing performances

Process	Main cause
Diffusions	Surface reaction
Bulk oxygen diffusion in grains	Adsorption/desorption
Inter grain oxygen diffusion	Reduction/oxidation
Gas diffusion inside the metal metrics	Catalysts
Surface diffusion of adsorbed species	Chemical reaction (change in composition)
	Charge transfer between adsorbed species and the bulk

**Fig. 8** The processes and their effect in MOXs gas sensing.

Physical and Chemical Factors Affecting to the Sensing Performance

Gas sensing performances such as response, sensitivity, response and recovery times are changed by various processes (Table 2), which can occur at the surface and/or in the bulk of the sensing material. Indeed, these modify the surface and electro-physical properties of the MOXs are shown in Fig. 8 (Korotcenkov, 2008). In other words, gas molecules interact with MOXs either as donors or acceptors of charge carriers and change the resistivity of the MOXs. Moreover, these changes are depending on the majority carriers (electrons in n-type and holes in p-type), nature (reducing or oxidizing) of the analyte. However, the performances are significantly governed by several physical facts such as crystallinity, grain size, morphology, activated adsorption sites, defects, formation of heterojunctions, etc., (Lin et al., 2019). So, a meaningful description of key features that are drastically altering the sensing performance of MOXs gas sensors is useful.

Morphology

Gas sensing technology began with a thick film approach and it moved to porous thick films and later into thin films. Generally, rougher topology along with unique structure, high surface to volume ratio, and porosity are identified as the main roots for outstanding sensing performance (Wang et al., 2020; Choi and Chang, 2018). Besides, the response value strongly depends on the surface states. Accordingly,

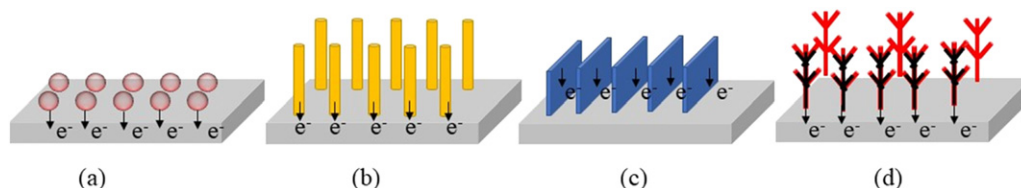


Fig. 9 Schematic of nanostructures; (a) 0-D; (b) 1-D; (c) 2-D; (d) 3-D heterostructures.

research on preparing materials with the higher surface state is gradually developed based on pioneer invention by Yamazoe (1991). Consequently, today, much research are devoted to preparing low dimensional nanostructures (Fig. 9(a-d)) such as 0-dimensional (nanoparticles; NP, quantum dots) (Umar *et al.*, 2021; Yu *et al.*, 2020), 1-dimensional (nanowires, nanorods, nanotubes, nanobelts) (Moumen *et al.*, 2021; Galstyan *et al.*, 2021), 2-dimensional (nanosheets, nanoflakes) (Munasinghe Arachchige *et al.*, 2018; Galstyan *et al.*, 2022) and 3-dimensional (heterostructures) (Kaur *et al.*, 2021; Zhang *et al.*, 2020) to enhance the response of the sensors. 1-D nanomaterials transfer carriers only along the axial direction, resulting in a significant increase in carrier mobility, 2-D nanomaterials have a larger surface area to promote gas absorption, and porosity to promote gas penetration (Zeb *et al.*, 2021), while 3-D nanomaterials have their regular geometry, abundant pores and large specific surface area (Meng *et al.*, 2022). Also, core-shell structures (Lee *et al.*, 2018) and hierarchical structures (Tshabalala *et al.*, 2021) are interesting because of their capability of modulating the conduction channels for a smooth transfer of carriers without additional barriers.

Besides, quasi 1-D MOXs nanostructures have several advantages concerning other low dimensional counterparts. For example, dimensions comparable to the extension of surface charge region, superior stability owing to the high crystallinity, low-resistance paths to charge carriers, with percolative conduction paths featuring a much-reduced number of crystallite interfaces, tunability of the receptor function toward specific gases with possible surface functionalization and feasibility of field-effect transistors (FET) configuration, minimal energy consumption and low weight that make them the ideal for gas sensing applications (Comini and Sberveglieri, 2010).

Grain size

Indeed, grain size is another crucial parameter that drastically alters the conductivity of MOXs sensors (Mirabella *et al.*, 2021). The grain size significantly governs the sensitivity, hence the grain boundaries are also playing an important role. To understand this phenomenon, let's consider three sizes of grain that are compared with the space charge layer width ($2L_D$) as shown in Fig. 6(a-c). Accordingly, conductance is restricted by the Schottky barrier at the grain boundaries when the grain size is larger than that of the thickness of the space charge layer. Once, the grain size is equal to the thickness of the space charge layer, conductance is restricted by necks between the grains. In the third case, where the grain size is less than the thickness of the space charge layer, conductance is highly affected by every grain. In this case there is a full depletion of the grains. Almost all the carriers in the grains are trapped at surface states, hence conduction is supported only by a few thermal-activated carriers. Also, conduction paths between the grains are omitted hence conductivity decreases drastically. Once, MOXs interact with gas species a transition from not activated to strongly activated carrier density (space charge region or accumulation region) occurs resulting in a significant change in the conductance as shown in Fig. 6(d,e) (Comini and Sberveglieri, 2010).

Defect in the MOXs

There are many different types of defects such as point defects, edges, grain boundaries, and dislocations. Defects are unavoidable in material synthesis processes and therefore crucial in affecting the electronic properties and hence sensitivity and selectivity. Among these defects, surface vacancies (SVs) are strongly modulating gas adsorption (Kim *et al.*, 2015). Besides, defects are capable of modifying the bandgap of MOXs (Al-Hashem *et al.*, 2019). For instance, when an oxygen vacancy is formed, if it is fully ionized, two electrons will be released into the conduction band. Accordingly, a higher number of oxygen vacancy-related defects will increase the number of electrons available for the redox reactions, leading to higher responses (Zhou *et al.*, 2018; Jagadale *et al.*, 2018; Choi *et al.*, 2020). On the other hand, a grain boundary is a disordered atomic arrangement that makes its properties different from those of the grain interior. Thereby grain boundaries modify the transducer function of MOXs (Waclawik *et al.*, 2012). Also, the edge sites in the crystal structure should be taken into account when concerning the gas absorption dynamics. Usually, edge sites have more active sites than basal planes, ascribed to a different local stoichiometry, higher number of dangling bonds and higher roughness which significantly enhance the gas absorption hence higher response in the sensor (Zeng *et al.*, 2018).

Functional modification of the MOXs

A functional modification includes metal cation doping, noble metal (Pt, Au, Ag, Nb)/metal oxide (PdO) surface loading, and semiconductor oxide composite formation to enhance the catalytic activity (Ziadi *et al.*, 2020), electrical conductance (Chen *et al.*, 2019; Zeb *et al.*, 2021), effective surface area (Lee *et al.*, 2020; Ko *et al.*, 2020). Besides, functional modifications are proficient in improving desirable properties or by reducing/eliminating existing challenges affecting the following characteristics:

- (1) microstructure and morphology (Wang *et al.*, 2010)
- (2) stoichiometric solid solution (Kolmakov *et al.*, 2008)
- (3) activation energy (Saruhan *et al.*, 2021)

Table 3 Effect of prominent features on the gas sensing performances for MOXs sensors

Features	Response	Sensitivity	Selectivity	Response/Recovery time	Stability
Morphology	✓				✓
Crystal orientation			✓		
Doping	✓	✓	✓	✓	✓
Surface modification	✓	✓		✓	✓
Working temperature	✓		✓	✓	
Poisoning	✓	✓	✓	✓	✓
Grain size	✓	✓			
Defects	✓				

(4) oxygen vacancies (Saruhan *et al.*, 2021)

(5) electronic structure (Li *et al.*, 2020)

Generally, two categories; surface and bulk functional modification are possible for MOXs. Once, surface functionalization (metal loading) is employed, a tiny Schottky junction is formed between the metal NP/nanocluster and the surfaces of the MOXs. As a consequence, metal NP/nanocluster becomes an electronegative surface. Once, gas interaction occurs, this high resistance is becoming more conductive because of electron transfer between metal NP/nanocluster and gas molecules resulting in a drastic change in the sensing performance including, sensitivity, selectivity, fast response/recovery time, lower working temperature.

Bulk doping is another direct and successful approach to enhance gas sensing performance of the MOXs which involves modifying acceptor or donor states, original crystal parameters, and bulk or surface Fermi level. Furthermore, doping is capable of removing electrons from the top of the valence band or injecting electrons to the bottom of the conduction band, modulating the forbidden bandwidth of the MOXs materials. Today, many metallic dopants such as Mn, Al, Co, Cr, Ni, Zr, Nb, W, Cu, Fe, and Y have been widely integrated into MOXs to improve gas sensing properties by changing the surface potential, surface chemistry, pure crystal phase of pristine materials.

Working temperature

In real applications, different reactive gases are present instantaneously in the same atmosphere and can interact with the sensor sensing element, therefore selectivity is a key feature in a real application. Regrettably, MOXs sensors have low selectivity due to the intrinsic sensing mechanism. Thermal activation of the sensing element is a fascinating approach to increase it. In brief, each gas has its own optimum catalytic oxidation (or reduction) temperature. As a consequence, different gases react at different rates and possess different response values based on the working temperature (Radhakrishnan *et al.*, 2021).

Accordingly, MOXs sensors can be tuned to detect the analyte gas more accurately (Wong *et al.*, 2019). For instance, Cr-incorporated Co₃O₄ NRs are capable of detecting xylene at a working temperature of 250 °C and toluene at 300 °C (Jeong *et al.*, 2014). Table 3 shows a short summary of how the sensing performance is changed by the prominent influencing features.

Stability of the MOX Gas Sensors

Gas sensors work at specific temperatures to detect targeted gas accurately. So, each sensor component is responsible for its long-term stability and reliability. Thereby, any tiny fault that transpires in the sensor design at any stage affects its stability, which is a crucial parameter of sensors when concerning real market applications. The stability of a sensor can be discussed in two means. One is reproducibility (active stability) of the sensor's performance during a certain period at its optimal working conditions. The second is retaining the sensitivity and selectivity during a period at normal storage conditions like room temperature and ambient humidity. However, the stability of a conductometric sensor is hindered by several facts such, as structural changes, poisoning, phase transformation, degradation of contacts and heaters, bulk diffusion, errors in design, change of humidity, and fluctuations of temperature in the surrounding atmosphere (Dey, 2018). The factors influencing stability can be divide into two groups based on technological and fabrication process issues. Accordingly, different approaches can be employed to minimize them as shown in Fig. 10. A detailed description can be found in Korotcenkov *et al.* (Korotcenkov and Cho, 2011).

Gas sensors Based on Other Sensing Methods

Today, several gas sensing methods are available (Fig. 2). Thus, the most active methods and their sensing mechanisms of gas sensing are briefly described here to provide a complete idea about the existing gas sensing technologies.

Gas Sensors Based on Optical Properties

The idea of preparing optical gas sensors started with the discovery of absorptivity of infrared (IR) light and ultra-violet (UV) radiation by some gases frequently used in the industries and present in the environment. A detailed list of these gases and the reason for detecting specific gas is reported by (Bogue, 2015). Usually, gas molecules absorb UV/visible (200–400 nm), near-

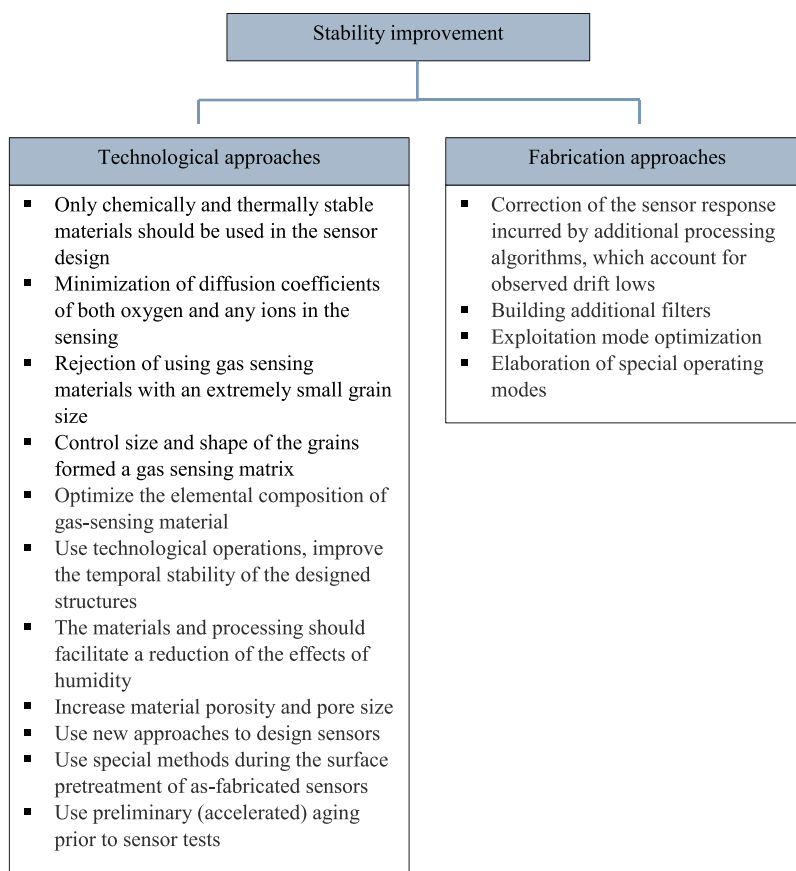


Fig. 10 Factors affecting the stability of the MOXs sensors.

infrared (700 nm–2.5 μm) or mid-infrared regions (2.5–14 μm) of the electromagnetic spectrum and show characteristics electronic transitions in UV/visible region and overtones of fundamental vibrations in mid-IR in the infrared region, that can be detected by several absorption techniques. For instance, non-dispersive infrared (NDIR), UV absorption, Fourier transform infrared (FTIR). In the simplest explanation, the operating principle of absorption-based techniques are based on the Beer-Lambert absorption law, $I = I_0 \exp(-\alpha L)$, where I_0 is the intensity of the incident light, I is the intensity of the light that has passed through the sensor/cell, α is the absorption coefficient of the gas and L is the optical path length. In contrast to absorption-based techniques, chemiluminescence (CL) is based on the intensity of the emitted light when the target analyte is being collided with a known compound where the intensity is proportional to the concentration of the gas. Besides, in UV fluorescence (UVF) a UV light (190–230 nm) is irradiated on the gas molecules and measure the intensity of the emitting UV light wavelengths (230 and 420 nm) where the intensity of this fluorescence is proportional to the gas concentration. The third category optical gas sensor, photoionization detector (PIDs) uses a deep UV light source to break the gas molecules or vapor into positively charged ions that result in a current flow between electrodes where current is proportional to the concentration of the gas or vapor concentration.

Gas Sensors Based on the Colorimetric Method

Colorimetric sensors detect elements by measuring absorbance or fluorescence spectra shift. Typically, dyes and other organic compounds which is built of aromatic structures (have many conjugated pi-systems) are used in the colorimetric gas sensors. These sensors are based on four different sensing mechanisms such as ring-opening and closing reactions, change of functional groups, ligand exchange, and phase transition (Cho *et al.*, 2020). The sensors in the first category are based on the shift of the absorption spectra due to the modulation in the length of the conjugated pi-system once its electron captures a specific photon. The second method is based on the change of the color of the dye or organic compound once its functional group reacts with the targeted gas. Besides, transition metal complexes have color due to electronic transitions in the energy level of d orbitals. Thus, the electrons in the d orbital can be modulated by engineering ligands around the transition metal ions. Accordingly, d orbital electrons are interacting with the electron clouds of the ligand and become non-degeneracy of electrons state. Once ligands are modified or substituted by the targeted gas molecules, the state of electrons in the d orbital is modulated and absorbs different wavelengths of light resulting in color variation in the ligand exchange based sensors. Also, phase transition-based sensors are operating on the principle of variation of color due to changes in the phase of the sensing element when it interacts with the gas molecules. Accordingly, specific catalysts are used in the sensing element to interact with the target gas resulting in

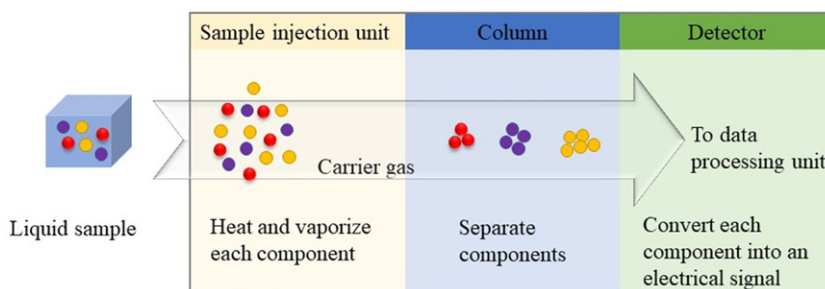


Fig. 11 Schematic of the gas chromatography (GC).

color change. For instance, when the iron is exposed to the ambient air its color is varying from gray to brown due to oxidation. Nevertheless, four different sensing mechanisms are available on colorimetry sensors, they are still very limited in gas sensing applications due to the difficulties in the detection of gaseous and toxic substances effectively.

Gas Sensors Based on the Gas Chromatograph

Gas chromatography (GC) is an analytical technique used to identify components that are vaporized by heat within the sample injection unit. Typical GC consists of three major sections.

- (1) sample injection unit - heat the sample and vaporizes
- (2) column - separate each compound
- (3) detector - detect the compounds and outputs their concentrations as electrical signals

Usually, a high purity (99.995%) carrier gas (inert gas such as helium, hydrogen, nitrogen, argon) always flows in sequence from the sample injection unit to the column, and then to the detector as shown in [Fig. 11](#). This carrier gas is responsible for transporting the target components that were vaporized in the sample injection unit to the column. However, efficiency in the column depends on the type of carrier gas used and its analysis conditions (linear velocity). So, the carrier gas is controlled by modulating pressure, column flow rate, and linear velocity. Also, there are two types of sample injection methods call hot and cold injection together with limitations in the sample injection volume (liquid 1–2 μL and gas 0.2–1 mL). Furthermore, to separate compounds two types of columns (packed columns and capillary columns) are used in GS where packed columns produce broad peaks spectrum and capillary columns produce sharp peaks spectrum. In addition, capillary columns produce taller peaks, which allows the detection of lower concentrations (high detection sensitivity). The third, most important part is the detector. They are divided into general-purpose detectors and selective, high-sensitivity detectors. Flame ionization detectors (FID), thermal conductivity detectors (TCD), barrier discharge ionization detectors (BID) are categorized into the first category while electron capture detectors (ECD), flame thermionic detectors (FTD), flame photometric detectors (FPD), and sulfur chemiluminescence detectors (SCD) are categorized into the selective, high-sensitivity detectors category. Accordingly, each detector has its working mechanism that has been reported in ([Instruments, 2022](#)).

Gas Sensors Based on Acoustic Methods

The concept of an acoustic sensor started with the quartz crystal microbalance (QCM) ([Sauerbrey, 1959](#)). This sensor works on the principle of resonant frequency modulation. In short, once the mass is loaded on the quartz crystal, the resonant element of an oscillator circuit, by adsorbed species the initial frequency is changed leading to an easily measurable frequency shift ([Cheeke and Wang, 1999](#)). The idea has been extended to surface acoustic wave (SAW) devices. In short, when an acoustic wave is propagating through or on the surface of the selective layer (receptor) its initial propagating path is changed due to the variation in mass and thickness of the receptor film. These changes arise as the sensor is exposed to the analyte. Such variation in propagating path alters the velocity/amplitude/phase of the propagating wave ([Fig. 12](#)). These variations in the propagating wave are monitored and correlated to a corresponding physical quantity such as an electrical signal. Accordingly, the first acoustic gas sensor was discovered in 1964 ([King, 1964](#)). Today, there are different types of configurations such as bulk acoustic wave (BAW), surface acoustic wave (SAW), flexural plate wave (FPW) device, thin rod or fiber acoustic wave (FAW), tube acoustic wave device, transverse wave devices, and cantilever beam structures are used in acoustic sensor with their advantages and disadvantages ([Cheeke and Wang, 1999](#)).

Gas Sensors Based on Catalytic Methods

Catalytic gas sensors are engineered on basis of catalytic combustion (oxidation). The first catalytic combustion type sensor was discovered by Jonson in 1923 ([Firth et al., 1973](#)). Till now, these sensors are the leader in detecting methane in the coal mine industry since 1959. There are two configurations for catalytic sensors; pellistors type and thermoelectric type gas sensors. Typically, these sensors consist of a detector cell and a reference cell. Usually, the detector cell is a platinum wire or coil to which

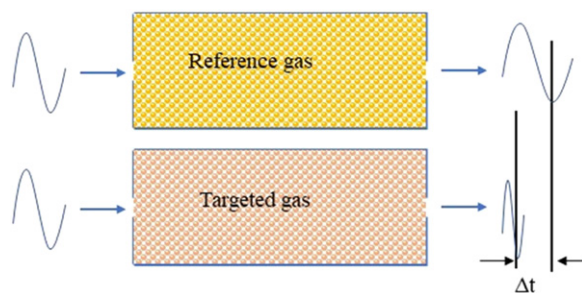


Fig. 12 Schematic of the working principle of acoustic wave sensors.

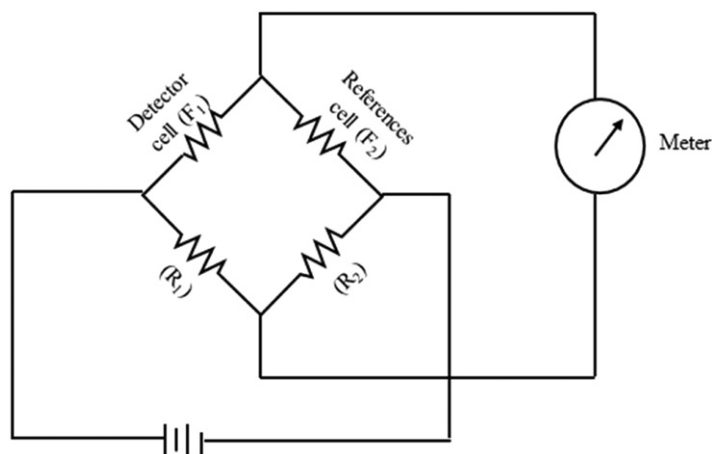


Fig. 13 Wheatstone-Bridge circuit configuration in the catalytic type gas sensors.

the carrier is attached, and it is coated with an oxidization catalyst such as alumina. When the sensor is exposed to combustible gas, the gas starts burning when they reach their ignition temperature. The reference cell is essentially an identical platinum coil, that has been treated to prevent combustible gas from igniting upon contact. However, both the configurations are based on one common working principle of the Wheatstone-Bridge circuit as shown in Fig. 13. Usually, the detector cells F_1 and F_2 are designed to hold equal electrical resistance when combustible gas is absent. Therefore, the bridge circuit will be in an equilibrium state where $F_1 \times R_1 = F_2 \times R_2$. Once, combustible gas burns in the detector cell, the electrical resistance increases with the combustion heat breaking the equilibrium of the bridge circuit. Accordingly current flows through the meter.

Gas Sensors Based on Capacitive Methods

Capacitive type chemical sensors (chemicapacitor sensors) are based on the change in capacitance due to modifications in dielectric constant/electric field or a change in thickness of the active layer when gas molecules are adsorbed. Usually, capacitance is known as; $C = \epsilon_o \epsilon_r A / d$ where ϵ_o is the permittivity of vacuum, ϵ_r is the relative permittivity, A is the area of an electrode and d is the distance between electrodes. Furthermore, the space between electrodes is filled with the dielectric layer and therefore d is its thickness. Usually, variation in any of these parameters causes changes in the capacitance. However, for a given device variation of the electrode area is negligible. Accordingly, chemicapacitor sensors are based on the principle of variation of relative permittivity or dielectric medium thickness. Furthermore, most of the inorganic gases have similar relative permittivity, resulting in poor selectivity in these chemicapacitor sensors. Accordingly, most of the real chemicapacitor sensors are based on the variation of the dielectric thickness (d) since d is significantly modulated by the concentration of the target gas, and the electronic interaction between the target gas and the semiconductor.

Gas Sensors Based on Cantilever Methods

Cantilevers, one of the elementary types of mechanical sensors, have been continually developed in a variety of dimensions and designs. These sensors are currently engaged in many applications. Typically, a cantilever is observed as a rectangular bar-shaped structure that is longer than it is wide and has a thickness that is shorter than its width or length. It is a horizontal structural element supported only at one end on a chip body; the other end is free. Usually, cantilevers are built-in silicon, carbon-based (graphene and carbon nanotubes), semiconductors (III-V nitrides: AlN and GaN), and polymer materials. The working principle of microcantilevers (MC) gas sensors is constituted by the mechanical actions and deformations of their micromachined components

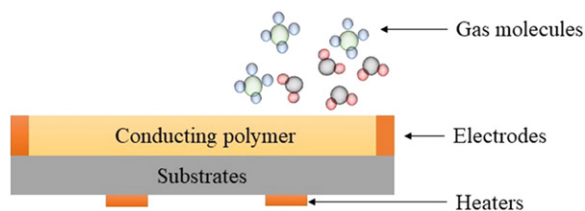


Fig. 14 Schematic of the chemiresistor conducting polymer sensor.

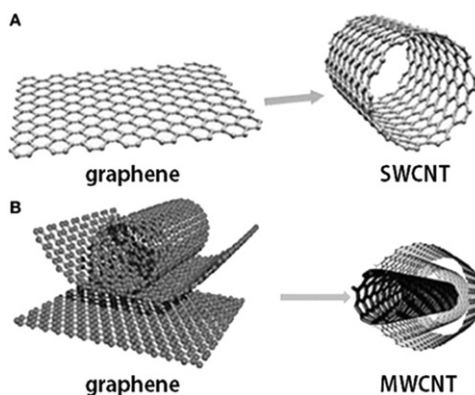


Fig. 15 Categories of CNTs. Reprinted with from Vidu, R., Rahman, M., Mahmoudi, M., *et al.*, 2014. Nanostructures: A platform for brain repair and augmentation. *Frontiers in Systems Neuroscience* 8.

subjected to the gas analyte. Also, the operational mode of an MC can be defined as either dynamic or static based on measured parameters, resonance frequency, or cantilever bending respectively (Long *et al.*, 2013). Once functioned in resonance mode, they are capable of detecting ultra-small masses with very high accuracy which is used in highly sensitive environmental or biomedical sensing devices (e.g., gas, DNA protein particulate matter, and cells) (Kelling *et al.*, 2011). Consequently, different transducers are used to identify the output signal, including electrical and optical conversion methods.

Conducting polymer-based gas sensors

Conducting polymers are a class of materials that not only exhibit electrical properties, but also exhibit magnetic, optical, wetting, mechanical, and microwave-absorbing properties to some extent (Das and Prusty, 2012). The primary investigations of conducting polymers began in 1977 (Torad and Ayad, 2020). The electrical conductance of the conducting polymers is significantly varying upon exposure to diverse organic and inorganic gases. Typically, π -conjugate structured conducting polymers show p-type conductivity. Accordingly, their conductivity is modulated by the interaction with gas molecules (an electron donor or acceptor). Therefore, conducting polymers are exploited as conductometric gas sensors since the early 1980s (Nylander *et al.*, 1983) (Fig. 14).

The polymer electrical conductance is also dependent on the preparation method and film thickness (Stussi *et al.*, 1997). In addition, hydration of the polymer and interface between the conducting polymer and the insulating substrate (glass, sapphire, quartz) are modulating the overall conductivity of the sensor (Wang *et al.*, 1999). However, the conductance of the polymer is significantly changed by active functional groups in their structure and adsorption mechanism (Liu *et al.*, 2012). Accordingly, polyaniline (PANI), polypyrrole (PPy), polythiophene (PTH), polyacetylene (PA), and poly(3,4-ethylene dioxythiophene) (PEDOT) is the widely used polymers in gas sensors to detect NO_x (Gusain *et al.*, 2017), SO₂ (Xu *et al.*, 2021), H₂S (Duc *et al.*, 2020), CO (Paul *et al.*, 2009), CH₄ (Wong *et al.*, 2019), NH₃ (Joshi *et al.*, 2011), CO₂ (Chen *et al.*, 2012). However, for their practical application further optimization is needed to decrease the high affinity toward volatile organic compounds (VOCs) and their relatively low conductivity. Moreover, water molecules are affecting to stability, sensitivity, and selectivity. Accordingly, enhancement in the active surface area, functionalization, redox doping, and preparing low dimensional conducting polymers such as nanofibers are under investigations as in the case of MOXs sensors.

Carbon nanotube (CNT)-based gas sensors

Nanotechnology is now regarded as the key to solving many barriers that are hindering sensitivity, low cost, portable sensors, and low power consumption. Consequently, carbon nanotubes, discovered by Iijima in 1991 (Iijima, 1991), have achieved significant interest due to their unique geometry, morphology, and properties. So, preparation and its electronic, mechanical, thermal, and optical properties are intensively and widely studied in many fields including gas sensors (Wang and Yeow, 2009). CNTs are graphene sheets of covalently bonded carbon molecules rolled into hollow cylinders. These CNTs are categorized into two groups; single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) (Fig. 15). Usually, SWNTs have a single

carbon layer with a diameter of 1–5 nm and MWCNTs have multiple layers of carbon (with an interlayer spacing of 3.4 Å) that are concentrically nested together (Zhang *et al.*, 2008). Interestingly, SWCN is p-type semiconducting while MWCNT shows metallic electronic properties similar to metallic SWNTs. However, the gas sensing properties of the CNTs largely depend on defect sites and surface properties. For instance, a higher surface area increase the absorption of a large amount of gas molecules, resulting in higher sensing properties. For this reason, preparing hybrids CNTs and metal oxide composites with CNT and their functionalization with noble and metal oxide are extensively employed to enhance their sensitivity.

Future Directions

Different gas sensors have already been commercialized. Concerning MOX gas sensors, in their bulk forms still suffer from several challenges such as lack of selectivity, high working temperature, slow response. However, the MOXs gas sensors have their unique intrinsic electrical, chemical, physical and optical, properties which attract researchers to integrate them in high-performing and reliable devices for advanced applications such as breath analysis, wearable technologies, environmental monitoring, food quality monitoring. Accordingly, many research works have been successfully employed to prepare various morphologies, crystal structures, nanostructures that are capable of detecting many gases, such as H₂, NO₂, NO, SO₂, CO, NH₃, H₂S, and several VOCs with high sensitivity, selectivity, and stability at a broad working temperature range.

The advancements in nanotechnology brought a new horizon for the conventional MOXs gas sensors. In which morphology is vastly modified as 0D, 1D, 2D, hierarchical, and heterostructures. Accordingly, nanostructured MOXs are ideal for future gas sensing applications because of their surface charge region, superior stability owing to the high crystallinity, low-resistance paths to charge carriers, tunability of the receptor function toward specific gases with possible surface functionalization and minimal energy consumption, and low weight. Among these morphologies, 1D MOXs structures would be the best choice in the next generation MOXs gas sensors because of their potential of fast electron transport, large active surface areas, and long-term stability which drastically enhance the sensitivity, response/recovery time, and stability of the sensor.

Concerning the fabrication of the devices, recent advancement in novel technologies has drastically changed the overall architecture and their size resulting in smaller as well as reducing the infrastructure support day by day. These innovations are very useful in integrating wearable and gas sensing devices in smartphone for environmental monitoring to aware people about the air quality, which indeed help to avoid many health issues as mentioned at the beginning of this article.

Conclusions

There are several sensing methods to detect toxic gases in the environment. Among these, metal oxide (MOX) gas sensors based on resistance modulation are interesting because of their cheap, simple configuration, easy setup. Accordingly, MOXs conductometric gas sensors have entered into the market. Indeed, with some deficiencies such as low selectivity, high working temperatures, slow response/recovery time. Thus, it is fascinating to rule out or hide these deficiencies for real applications. This article has described the overall architecture, gas sensing mechanisms, and factors affecting the sensing mechanism.

Gas sensing performances of MOXs conductometric sensors can be significantly improved by nanostructures and subsequent metal loading, bulk doping, constructing heterojunctions, and composites. Also, working environments such as humidity, and working temperature drastically affect their gas sensing performances, therefore for each material precise working conditions must be determined to optimize the final performances towards a specific compound.

The enrollment of novel technological approaches in designing, engineering will bring the MOXs into the smart and miniaturization devices in IOT, they will be wearable and cheaper together with superior reliability compared to those in the market today.

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Oxide Based Memristors: Fabrication, Mechanism, and Application

Amitesh Kumar, Mangal Das, and Shaibal Mukherjee, Indian Institute of Technology Indore, Simrol, Indore, India

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Introduction

Memristor has emerged as a potential candidate for non-volatile random access memory in recent times as an alternative to flash memory. Among all the probable alternatives for flash memory, resistive random access memory (RRAM), stands most promising owing to its simple structure, high switching speed, low power consumption, high stacking density etc. However, it has been almost half a century since the initial experimental observations of resistive switching (RS) behavior, however, the field of memristors is still at a very premature stage. Although, the concept of memristor proposed by Leon Chua in 1971 (Chua and Kang, 1976), the first experimental observation of RS phenomena in TiO_2 thin films, by Strukov *et al.* came in 2008. RS behavior has also been observed with wide band gap metal oxides such as TaO_x , NiO_x , ZnO containing regulated oxygen vacancies. Native *n*-type semiconductors such as ZnO (Kumar *et al.*, 2017), whose electrical properties are mainly governed by the presence of electrically active and stoichiometric native point defects, such as vacancies and interstitials are viable options to implement memristor structure (Mundle *et al.*, 2016). There are many theoretical models such as filamentary conduction theory (Huang *et al.*, 2013), homogenous ion transport phenomenon (Huang *et al.*, 2013), and Schottky barrier formation/dissolution (Li *et al.*, 2014) to explain memristive behavior. However, there is so much of variability of values of set/reset voltages and high resistance state (HRS)/low resistance state (LRS) ratio for memristors that it creates a lot of ambiguity about exact physical conduction mechanism for memristors.

Here, we have reviewed various aspects of memristors, which determine the recent progress in the field of memristors. After a brief introduction in terms of its physical understanding, we have discussed other aspects of memristors such as conduction mechanisms, structure and fabrication methods. Further, we have discussed various applications of memristors, besides being used as non-volatile memory. Cross-bar mechanism has been discussed to be the simplest structure for implementation of memristors for large-scale applications. Finally, the challenges and future prospects of memristors are discussed.

Physical Understanding of Memristor

Fingerprints of Memristor

Memristor is a state-dependent system which shows zero-crossing with pinched hysteresis loop with decrease in hysteresis loop area with increasing operation frequency (Chua and Kang, 1976). Leon Chua extended this theory for resistive switching memories, which behave like memristors (Chua, 2011). Since device possesses certain inertia, and cannot respond to fast variation in excitation waveform and therefore it settles to some equilibrium state, with decreased hysteresis loop area for higher sweep rates (Chua and Kang, 1976). It explains pinched current-voltage (I-V) hysteresis, loop as shown in Fig. 1(a) (Kumar *et al.*, 2017), which is observed to be dependent on bias sweep rate (Kumar *et al.*, 2017). It shrinks to smaller loop for higher sweep rates, conforming to memristive behavior (Chua and Kang, 1976; Chua, 2011), and (Wang *et al.*, 2010). Similar results are reported by Wang *et al.* to ratify memristive behavior (Wang *et al.*, 2010).

Performance Parameters

Major performance parameters of memristor as memory cell are its endurance and retention. Endurance depicts switching performance of memristors in terms of switching cycle, whereas retention does it in terms of time. Fig. 1(b) shows a RS device operated by set and reset pulses with a reading voltage of 0.2 V. The programming voltages for the HRS and LRS are 3 and -1 V, respectively. After 130 switching cycles, the $\text{Pt/Cu}_x\text{O}/\text{Cu}$ device has been observed to be deteriorated (Lv *et al.*, 2009). Aluminum (Al) top electrode is recommended for high endurance (Lv *et al.*, 2009) by Hangbing *et al.* Fig. 1(c) depicts endurance for $\text{Al}/\text{ZnO}/\text{Al}$ device (Kumar *et al.*, 2017), as reported by Kumar *et al.* HRS and LRS variations have been shown as a function of the number of switching cycles measured at a reading voltage of 0.1 V at room temperature (RT). As observed from figure, the variation of HRS and LRS during cycling is consistent without much degradation. High endurance is due to AlO_x formation/dissolution at $\text{Al}(\text{top electrode, TE})/\text{ZnO}/\text{Al}$, (Kumar *et al.*, 2017; Lv *et al.*, 2009). Further, the RS retention characteristic for same device is shown in Fig. 1(d) (Kumar *et al.*, 2017) using a small reading voltage of 0.1 V. No significant switching degradation after the duration 1×10^6 s (11 days) is observed, which is extrapolated to 10 years for non-destructive readout, (Qi *et al.*, 2013; Bae *et al.*, 2016).

Fabrication Methods

Performance of any memory device primarily depends upon fabrication method. Important characteristics of any fabrication method to process memristors is to ensure consistent device performance parameters such as endurance and retention, with stable set/reset voltages and low forming voltages or no forming at all. Memristor follows symmetric/asymmetric structures in process of optimizing structural defects, using the bilayer structures or inserting nanocrystals upon an insulating layer, to control various performance parameters to make it viable for practical implementations. Basic structure of an RRAM follows Metal (TE)/ Semiconductor/Metal (Bottom electrode, BE) (MSM)

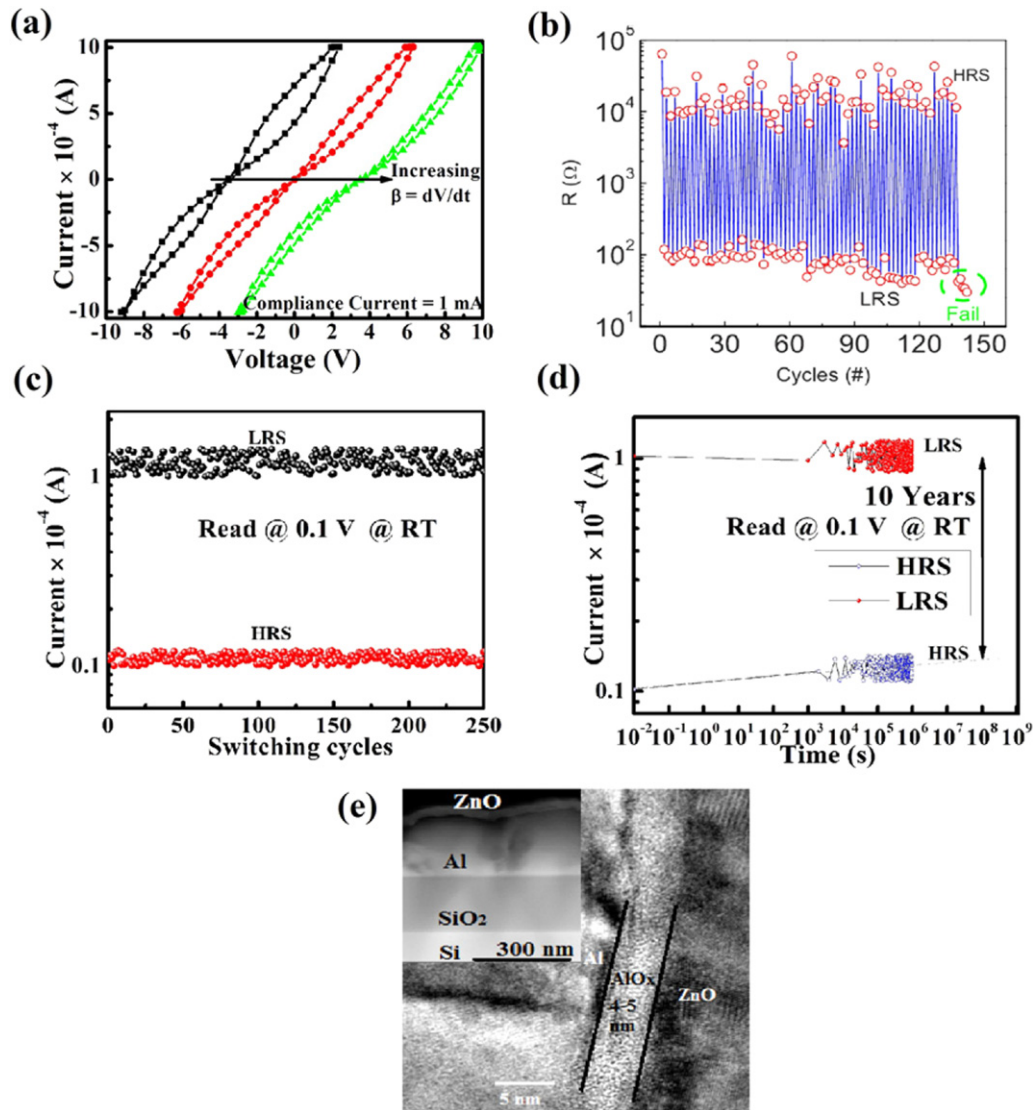


Fig. 1 (a) Pinched hysteresis loop for Al/ZnO/Al memory cell. (b) Device fails at LRS and never returns. Reproduced from Lv, H., Wang, M., Wan, H., *et al.*, 2009. "Endurance enhancement of Cu-oxide based resistive switching memory with Al top electrode". *Appl. Phys. Lett.* 94 (21), 213502. (c) Endurance for 250 cycles and retention for 10 years for Al/ZnO/Al memory cell. (d) Endurance enhancement with Al top electrode due to AlO_x interfacial oxide formation. Reproduced from Kumar, A., Das, M., Garg, V., *et al.*, 2017. "Forming-free high-endurance Al/ZnO/Al memristor fabricated by dual ion beam sputtering". *Appl. Phys. Lett.* 253509 (110), 1–6.

structure with similar or different TE and BE, with single or bilayer semi-conductor layer. Switching layer of memristor can either be of one single material, as reported by Kumar *et al.* using ZnO as single switching layer (Kumar *et al.*, 2017) or of bilayer switching hetero-structure. For bilayer heterostructure as the switching layer, both the layers may be grown by same fabrication method or different methods (Chen *et al.*, 2014). Zoofakar *et al.* have reported ZnO-based RS where upon radio-frequency (RF) sputtered ZnO seed layer, an electrodeposited layer has been grown to make a hetero-structure based switching layer (Zoofakar *et al.*, 2013). Table 1 provides an overview of different deposition techniques and corresponding device performance parameters to fabricate resistive memory cell based upon transition metal oxides (TMOs). Further, we discuss various fabrication methods and corresponding examples of RS devices fabricated through it.

ALD

A typical ALD reaction involves two reactants, a precursor and an oxidant (Zhang *et al.*, 2013). Film thickness can be controlled very well at even nanometer scale, and a high conformity can be achieved, which is particularly suitable for 3-dimensional (3D) memories constructed in the cross-bar architecture. Improvement of the RS performance is illustrated in TiO₂ by controlling deposition temperature and variation of deposition cycles of plasma enhanced ALD (PEALD) process, an enhanced variation of the standard thermal ALD, which allows to adjust the resistivity of the layers (Cho *et al.*, 2015).

Table 1 Comparative analysis of different methods for RS device fabrication and corresponding device parameters

Deposition technique	Material	D (nm)	T _s (°C)	Uni/Bi	Forming	Set/Reset Voltage (V)	Retention (s) /Endurance (cycles)	References
RF sputtering	Pt/ZnO/Pt	100	RT	Uni	Yes, 3.3V	— 2/ — 1	~ / ~	(Chang <i>et al.</i> , 2008)
	Pt/TiO ₂ /Pt	70	RT	Uni	Yes, 5V	2/1	10 ⁴ /3.72 × 10 ²	(Oh <i>et al.</i> , 2011)
	Pt/TaO _x /Pt	60	RT	Bi	Yes, 6V	2/ — 1.9	10 ⁴ /10 ¹¹	(Wu <i>et al.</i> , 2013)
Direct current (DC) sputtering	Al/ZnO/Si	60	RT	Bi	No	3.2/-3.2	~ / ~	(Chen <i>et al.</i> , 2012a)
	— Pt/Co-TiO ₂ /Pt	150	600	Bi	No	5/-5	10 ⁵ /800	(Hirose <i>et al.</i> , 2011)
	— Pt/NiO/Pt	150	300	Uni	Yes, 3.5V	3//—1	~ / ~	(Seo <i>et al.</i> , 2005)
Metal organic chemical vapor deposition (MOCVD)	ITO/ZnO/ITO	100	200	Uni	Yes, 3.2V	2.6/1.8	10 ⁵ /100	(Seo <i>et al.</i> , 2008)
Atomic layer deposition (ALD)	Pt/TiO ₂ /Pt	43	550	Uni	Yes, 7V	1.2/0.8	~ / ~	(Cao <i>et al.</i> , 2009)
	Au/HfO ₂ /Pt	39	400	Uni	Yes, 5 V	2/0.75	~ / ~	(Lee <i>et al.</i> , 2008a)
	AZO/ZnO/Al	50	220	Bi	Yes, 13V	10/—11	~ / ~	(Mundle <i>et al.</i> , 2016)
	Pt/TiO ₂ /Ru	20–57	~	Uni/Bi	~	2/1	~ / 10 ⁶	(Choi <i>et al.</i> , 2005)
Chemical bath deposition (CBD)	Ru/HfO _x /TiN	20	~	Uni	Yes, 5 V	NS	~ / ~	(Lee <i>et al.</i> , 2008b)
	Pt/ZnO/Pt	100	95	Bi	Yes, 3.4V	1.5/0.6	10 ⁴ /90	(Huang <i>et al.</i> , 2012)
	Pt/TiO ₂ /FTO	130	RT	Uni/Bi	Yes, 7 V	1.5/ — 2	10 ⁵ /100	(Zhang <i>et al.</i> , 2011)
Dual ion beam sputtering (DIBS)	Pt/Cr-ZnO/Pt	~	RT	Bi	No	3/ — 4	~ / 5 × 10 ⁴	(Xu <i>et al.</i> , 2014)
	Al/ZnO/Al	60	100	Bi	No	— 6.2/6.3	10 ⁶ /250	(Kumar <i>et al.</i> , 2017)

Source: RT: Room temperature D-thickness NS-No sharp V_{set} and V_{reset}.

MOCVD

MOCVD is a variant of chemical vapor deposition (CVD) (Lee *et al.*, 2008a; Rohde *et al.*, 2011), used for creating high purity crystalline semiconducting thin films and micro/nano structures. Precision fine tuning, abrupt interfaces, epitaxial deposition, and a high level of dopant control can be readily achieved. Seo *et al.* have reported ZnO based transparent resistive device fabricated by MOCVD at 200°C using diethylzinc as the metal source, H₂O as the oxidizer, and Ar as the carrier gas.

CBD

CBD (Chen *et al.*, 2017) includes a variety of routes for fabricating functional oxide films and coatings at relatively low temperature by immersing a substrate in a liquid solution (Cheng *et al.*, 2006). It can be employed for large-area batch processing or continuous deposition. Though, it is a simple and a very economical method of fabrication, repeatability of performance parameters of memory cells are major issues in this fabrication method (Cheng *et al.*, 2006). Huang *et al.* have reported CBD deployed ZnO based RS device with RF magnetron sputtered seed layer of ZnO (Huang *et al.*, 2012). Nanorods in this bilayer structure enhance the resistance ratio of device.

Sputtering

Sputtering (DC/RF/Reactive RF)

Besides DC magnetron sputtering (Chen *et al.*, 2012a), RF magnetron sputtering (Chang *et al.*, 2008) and reactive RF sputtering (Xu *et al.*, 2008) are reported to be other efficient methods to synthesize uniform, stable, highly crystalline and stoichiometric films yielding reproducible and durable RRAM devices. In these processes, ion beam is bombarded on a target material in a vacuum maintaining the RF power between 200W and 800W. RS devices based on ZnO (Chang *et al.*, 2008), TiO₂ (Oh *et al.*, 2011) etc. have been successfully fabricated by RF sputtering. The high-power prerequisites and contaminations inside deposition chamber are the major constraints of these processes as compared to ALD or PEALD.

DIBS

DIBS system is equipped with RF deposition ion source and direct-current coupled (DC) assist ion source (Singh *et al.*, 2016), as shown in Fig. 2(a). As compared to single ion beam deposition, the film stoichiometry is enhanced in DIBS by mixing oxygen into the working gas (Ar) in the assist ion source (Yoon *et al.*, 2005). DIBS deposition method is widely recognized to produce high-quality compound semiconductor films with reasonably better compositional stoichiometry, uniformity, and adhesion to the substrate surface. RF deposition source is widely used for deposition of oxides and semiconductors, although metals can also be grown. Assist ion source is employed to pre-clean the substrate surface before film deposition and to hinder three-dimensional island formation and remove weak dangling bonds during film deposition process, assisting in reduction of columnar growth of thin films and thereby enhancing growth uniformity and film adhesion to the substrate.

Kumar *et al.* have reported DIBS fabricated forming-free and high-endurance RS device (Kumar *et al.*, 2017). As compared to ALD, DIBS method is fast and does not need any ultra-pure volatile precursors. Further, DIBS as compared to many chemical deposition methods (Zoolfakar *et al.*, 2013; Huang *et al.*, 2012; Sun *et al.*, 2015), generates stoichiometrically more uniform and controlled

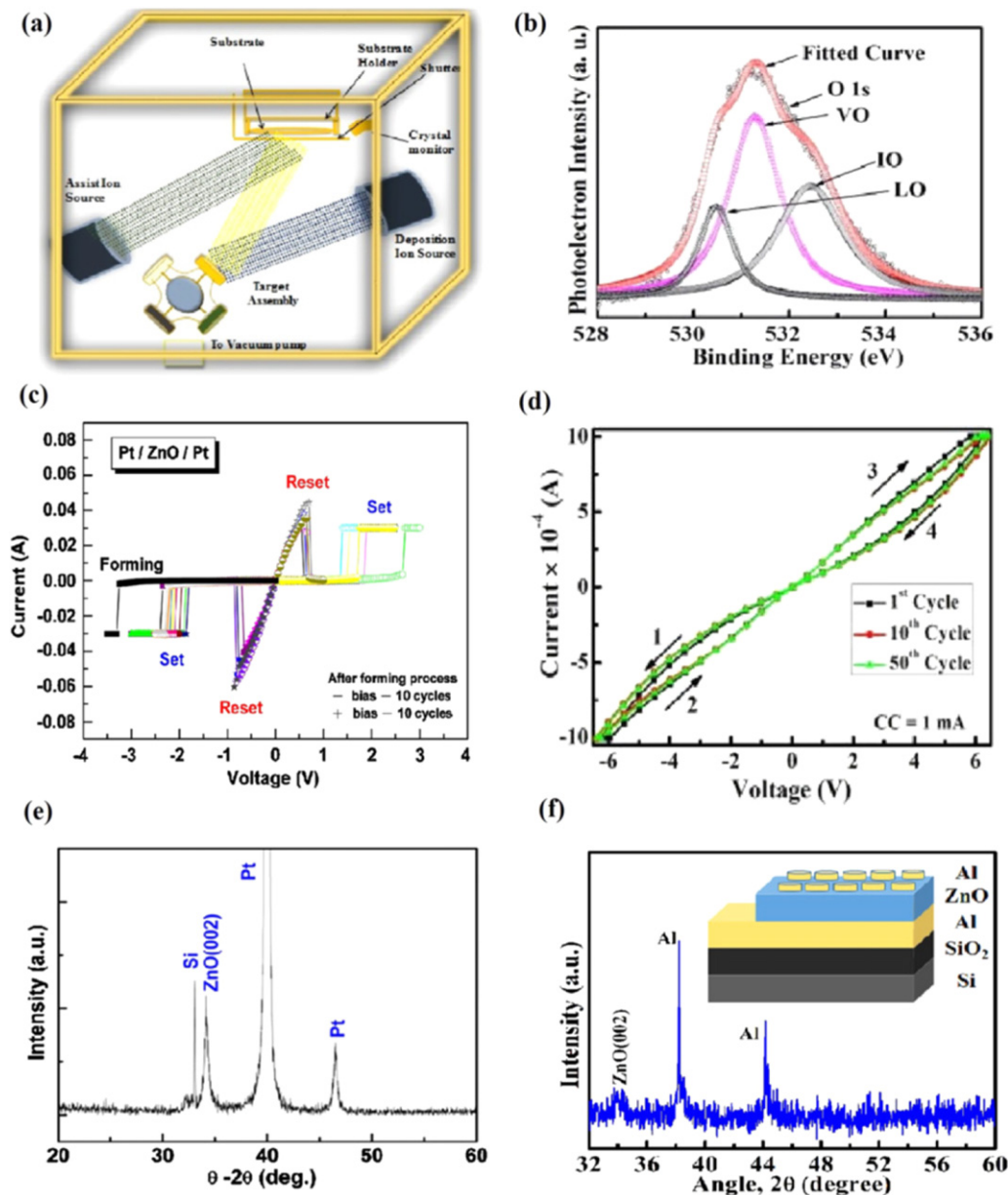


Fig. 2 (a) Schematic of DIBS, (b) X-ray photoelectron spectroscopy (XPS) spectra showing lattice, non-lattice oxygen ions and oxygen vacancies. (c) Forming of Pt/ZnO/Pt memory cell. (d) Forming-free memory cell Al/ZnO/Al. (e) Crystalline ZnO showing unipolar behavior. Reproduced from Chang, W.-Y., Lai, Y.-C., Wu, T.-B., *et al.*, 2008. "Unipolar resistive switching characteristics of ZnO thin films for nonvolatile memory applications". *Appl. Phys. Lett.* 92 (2), 22110. (f) Amorphous ZnO showing bipolar behavior. Inset displaying device schematic. Reproduced from Kumar, A., Das, M., Garg, V., *et al.*, 2017. "Forming-free high-endurance Al/ZnO/Al memristor fabricated by dual ion beam sputtering". *Appl. Phys. Lett.* 253509 (110), 1–6.

deposition. Moreover, DIBS system provides ease of fabrication of RS device as the number of defects in different regions of film can be suitably controlled by modifying oxygen partial pressure during thin film growth of mainly oxide based materials. Device has been fabricated at low temperature (100°C) and is also limited to 60 nm thickness, as compared to many other methods as illustrated in [Table 1](#). Performance of RS device is stable for low temperature fabrication and lower thickness of film ([Kumar *et al.*, 2017](#)).

Conduction Mechanism in Memristors

Switching mechanism of memristors depend upon various factors and aspects. Here, we review major resistive switching mechanisms of memristors. Later, we have discussed general electrical conduction mechanism of metal-insulator-metal (MIM) structure for HRS and LRS of memristor

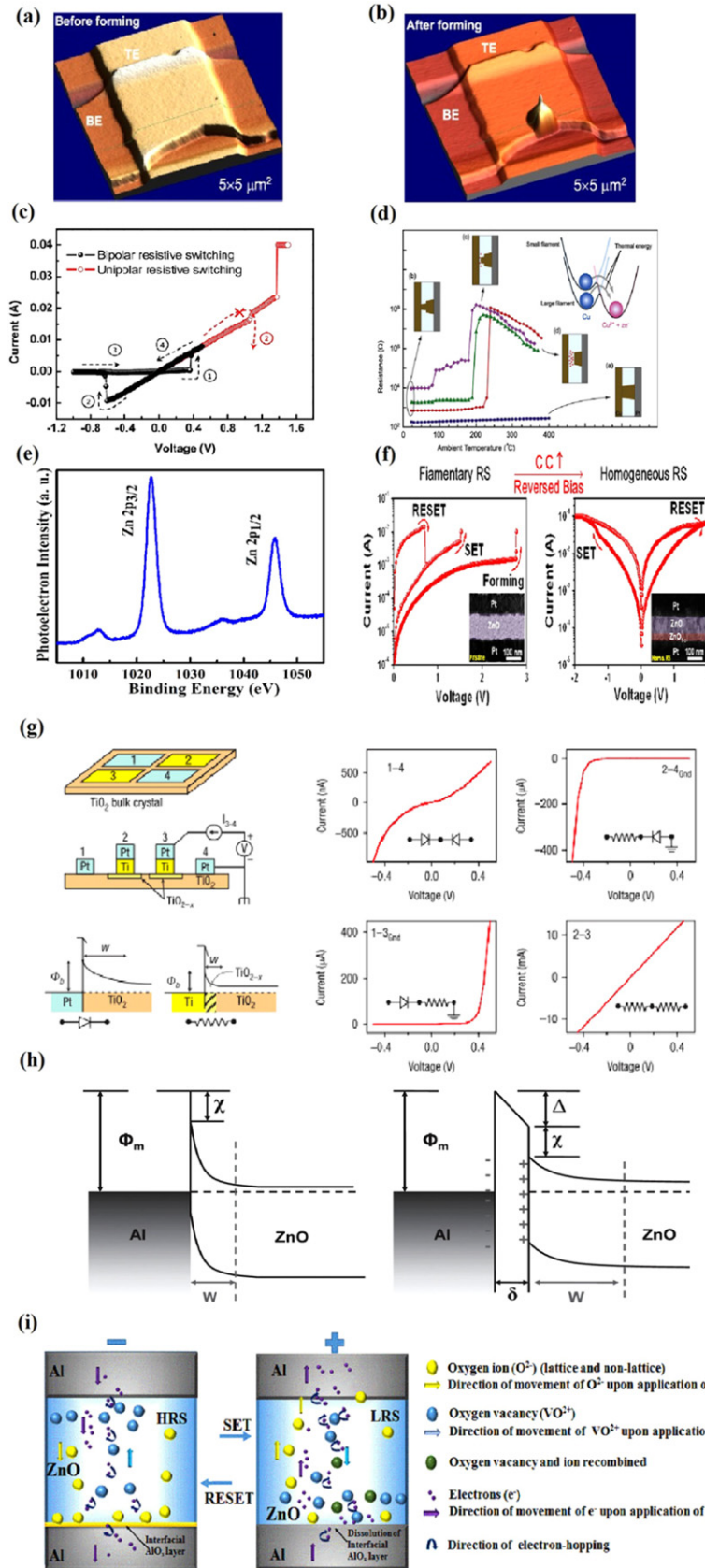


Fig. 3 Contact bubble formation illustration (a) before forming and (b) after forming. Reproduced from Yang, J.J., Miao, F., Pickett, M.D., *et al.*, 2009. "The mechanism of electroforming of metal oxide memristive switches". *Nanotechnology* 20 (21), 215201. (c) Bipolar and unipolar RS. Reproduced from Lee, S., Kim, H., Park, J., Yong, K., 2010. "Coexistence of unipolar and bipolar resistive switching characteristics in ZnO thin films." *J. Appl. Phys.* 108 (7), 2008–2011. (d) Cation migration. Reproduced from Tsuruoka, T., Terabe, K., Hasegawa, T., Aono, M., 2010. "Forming and switching mechanisms of a cation-migration-based oxide resistive." *Nanotechnology* 21 (42), 425205. (e) XPS of Zn in ZnO film. Reproduced from Kumar, A., Das, M., Garg, V.,

et al., 2017. "Forming-free high-endurance Al/ZnO/Al memristor fabricated by dual ion beam sputtering." *Appl. Phys. Lett.* 253509 (110), 1–6. (f) Transformation from homogeneous to filamentary. Reproduced from Huang, C.H., Huang, J.S., Lai, C.C., *et al.*, 2013. "Manipulated transformation of filamentary and homogeneous resistive switching on ZnO thin film memristor with controllable multistate." *ACS Appl. Mater. Interfaces*, 5 (13), 6017–6023. (g) Interface-limited conduction. Reproduced from Yang, J.J., Pickett, M.D., Li, X., *et al.*, 2008. "Memristive switching mechanism for metal/oxide/metal nanodevices." *Nat. Nanotechnol.* 3 (Suppl. 7), 429–433. (h) Schottky oxide barrier at Al/ZnO interface. Reproduced from Li, C., Beirne, G.J., Kamita, G., *et al.*, 2014. "Probing the switching mechanism in ZnO nanoparticle memristors." *J. Appl. Phys.* 114501, 1–17. (i) Co-existence of homogeneous switching and interfacial oxide formation/dissolution. Reproduced from Kumar, A., Das, M., Garg, V., *et al.*, 2017. "Forming-free high-endurance Al/ZnO/Al memristor fabricated by dual ion beam sputtering." *Appl. Phys. Lett.* 253509 (110), 1–6.

Resistive Switching Mechanism

Switching mechanism of RS depends upon structural and electrical properties, which are governed by the concentration of defects in thin film. To analyze the concentration level of defects in the film, XPS spectra and photoluminescence (PL) characterization can be deployed as illustrated by Kumar *et al.* (Kumar *et al.*, 2017). XPS spectra of O 1s can be observed in Fig. 2(b). Besides, O atoms at regular lattice site (LO), O atoms in the oxygen deficient regions (VO) in ZnO (Pandey *et al.*, 2013) show significant level which attributes to presence of oxygen vacancies (VO) in ZnO. These high amount of VO have significant roles in the realization of forming-free RS (Mao *et al.*, 2010; Lee and Tseng, 2014), Mao *et al.* have reported VO pre-existing in ZnO films playing an important role in the realization of forming-free cells (Mao *et al.*, 2010). High content of non-lattice oxygen ions O^{2-} (IO) existing in ZnO assists recovery of VOs during the reset process (Xu *et al.*, 2008) and ensures stable switching characteristics. Nuo *et al.* have reported generation/recovery of VOs and presence of non-lattice oxygen ions playing a critical role in resistance switching (Xu *et al.*, 2008).

Forming

In general, high voltage forming process, as illustrated in Fig. 2(c), is required to make the device conducting (Chang *et al.*, 2008). A forming-free cell as compared to a forming-necessary cell shows more stable RS characteristics and also avoids destruction of electrodes (Huang *et al.*, 2016). Although Sun *et al.* have reported forming-free ZnO based memory cells but it requires post-processing steps in the form of hydrogen surface annealing (Sun *et al.*, 2015). Forming-free ZnO based memory cells, as reported by Fatih *et al.*, have larger thickness of RS material of 300 nm (Gul and Efeoglu, 2016). However, lower thickness is preferable for RRAM cells, (Sun *et al.*, 2015; Strukov *et al.*, 2008a). The values of V_{set} and V_{reset} of the forming-free (Chen *et al.*, 2012a) memory cell reported by Chen *et al.* are not stable. However, in case of device as fabricated by DIBS by Kumar *et al.* (Kumar *et al.*, 2017), a stable set and reset voltages for device cut-off for forming-free memory cell have been reported, as demonstrated in Fig. 2(d). The crystalline ZnO film, as shown in Fig. 2(e), in which forming is necessary to make it conducting (Chang *et al.*, 2008). Whereas Al/ZnO/Al device (Kumar *et al.*, 2017) shows forming-free behavior with good reversibility and stability of the switching response, and continuously switches between its ON (LRS) and OFF (HRS) states for 50 cycles (Fig. 2(d)). The amorphous film, as depicted in Fig. 2(f) (Inset showing schematic of device), is suitable for forming-free behavior of the device (Huang *et al.*, 2016).

Further during high voltage forming process, contact bubble formation and electro-deterioration phenomena are generally observed as illustrated in Fig. 3(a) and (b) (Yang *et al.*, 2009). Generally, usage of Pt electrodes in RRAM suffer from switching degradation (Lv *et al.*, 2009) and deformation of junction (Yang *et al.*, 2009) due to oxygen bubble formation at metal/semiconductor contact. Contact bubble formation in Al electrodes is avoided owing to AlO_x interfacial oxide formation (Kumar *et al.*, 2017). Besides, Al electrodes is economical as compared to Pt and also promotes high endurance (Chen *et al.*, 2012a).

Unipolar and bipolar RS

RS is classified as unipolar RS (URS) (Fig. 3(c)) or bipolar RS (BRS) (Fig. 3(d)), according to whether switching is dependent on the operating voltage polarity or not (Lee *et al.*, 2010). URS does not depend on voltage polarity, so URS can be observed with a single voltage polarity. BRS, on the other hand, is completely dependent on voltage polarity, so set and reset processes are operated using opposite voltage polarities. Generally either URS (Chang *et al.*, 2017) or BRS (Kumar *et al.*, 2017) is reported for a single system with various mechanisms being suggested to explain each phenomenon. On the other hand, both URS and BRS have been induced in some materials by changing factors such as compliance current (I_c) or the properties of the films (Lee *et al.*, 2010), as shown in Fig. 3(c) where I_c governs the transition between two switching. Table 2 depicts unipolar or bipolar conduction behavior in RS devices with corresponding materials.

Ion migration

Among the widely accepted RS mechanism, ion migration is most common. There are two types of ions: cations and anions, and they migrate in opposite directions under the influence of an external electric field. In a material like ZnO, where oxygen ions as anions may participate in anion migration based switching, or it may occur that Zn^{2+} participates in cation migration based switching (Tang *et al.*, 2012). Ions may migrate to form and dissolve filaments in terms of filamentary conduction (Huang *et al.*, 2013; Muenstermann *et al.*, 2010), or they may move homogeneously throughout the medium as homogeneous conduction, (Huang *et al.*, 2013; Xu *et al.*, 2014).

Filamentary conduction

Filamentary conduction may be due to vacancy/ion filament formation/annihilation. Besides, anion migration (Kumar *et al.*, 2017), cation (metallic ion) migration also contributes to filament formation/annihilation (Tsuruoka *et al.*, 2010a). Fig. 3(d) shows Cu^{2+} ion migrating to form conducting filaments as suggested by Tsurukova *et al.* (Tsuruoka *et al.*, 2010b). In case of ZnO, being enriched

Table 2 RS types based on polarity and corresponding conduction mechanisms and materials

Type	Corresponding conduction	Switching materials
URS	Filamentary conduction	ZnO, (Chang <i>et al.</i> , 2017) TaO _x (Zhang <i>et al.</i> , 2010)
BRS	Filamentary conduction	TiO ₂ , (Tsunoda <i>et al.</i> , 2013; Do <i>et al.</i> , 2010)
	Homogeneous conduction	ZnO, (Kumar <i>et al.</i> , 2017; Chen <i>et al.</i> , 2012a)
	Interface limited conduction	ZnO (Kumar <i>et al.</i> , 2017)
URS and BRS	Filamentary conduction	ZnO, (Lee <i>et al.</i> , 2010) TiO ₂ (Jeong <i>et al.</i> , 2007)

with oxygen vacancy (VO) related defects, generally anion migration is recognized to be the governing switching mechanism (Kumar *et al.*, 2017). To ensure this, XPS spectra of Zn 2p levels in ZnO has been analyzed by Kumar *et al.* Zn 2p_{3/2} and Zn 2p_{1/2} levels have their XPS peaks corresponding to binding energy values at 1022.66 and 1045.72 eV, respectively, which are attributed to Zn atoms at regular lattice sites in ZnO bulk, as shown in Fig. 3(e). The binding energy variance of 23.06 eV is in agreement with previously reported values of Zn²⁺ ratifying fully oxidized state of Zn atoms, i.e., Zn²⁺. XPS spectra fit in to stoichiometric oxide layer of ZnO. This supports absence of any free metallic zinc ions, which disproves probability of any metallic ion conduction.

Homogeneous conduction

In addition to filamentary resistive switching, there is homogeneous interface resistive switching, which behave as continuous switching, attributed to an asymmetric balance of Schottky-barrier heights induced by the electric field via trapping and de-trapping processes of carriers through defective states at interfaces between the functional material and electrode. The switching current via homogeneous switching greatly depends on the device area, which ensures an appropriate current to maintain a reliable device operation (Huang *et al.*, 2013). There may occur controllable transformation of filamentary to homogeneous interface RS in a ZnO thin film MIM structure via different bias polarities as illustrated in Fig. 3(f) (Huang *et al.*, 2013).

Interface-limited switching

In general, reactive metal-ZnO interfaces are found to generate extrinsic defects due to reactions and/or inter-diffusions against non- reactive interfaces. Oxides of reactive metals such as Al, Ti have far lower standard Gibbs free energy for formation as compared to that for ZnO and oxides of inert electrodes (Pt and Au) (Chen *et al.*, 2012a). Depending upon electrode behavior to be reactive/inert, barrier may appear or disappear, as illustrated in Fig. 3(g) and interface may behave Schottky/Ohmic (Yang *et al.*, 2008). Appearance of Schottky barrier at Al/ZnO interface during HRS has been illustrated in Fig. 3(h) (Li *et al.*, 2014). Stoichiometric modulation of the oxygen-rich region at interface of Al/ZnO introduces an asymmetric Schottky barrier height subduing current in a voltage range restricted to difference of barrier heights (Mundle *et al.*, 2016).

Co-existence of ion migration and interface-limited switching

Fig. 3(i) illustrates schematics of Al/ZnO/Al memory cell in HRS and LRS states, as suggested by Kumar *et al.* (Kumar *et al.*, 2017) depicting the roles of oxygen vacancy, oxygen ions, and AlO_x interfacial layer. Underlying RS mechanism as suggested by Kumar *et al.* is a combination of electron hopping through conduction paths in bulk and redox reaction leading to formation and dissolution of AlO_x layer at interface, (Rajachidambaram *et al.*, 2013; Brillson and Lu, 2011). The generation/recovery of oxygen vacancies and oxygen ions during the set/reset has a significant role in bipolar switching (Xu *et al.*, 2008). Sufficient non-lattice oxygen ions, favor recovery as well as assist in redox reaction at Al/ZnO interface (Xu *et al.*, 2008).

Conduction Mechanism in Metal-Insulator-Metal (MIM)

The conduction mechanism in metal-insulator (wide band gap semiconductor)-metal (as shown in Fig. 4(a)) (MIM) stacks can be roughly divided in two classes according to models for the (leakage) current:

- (1) Bulk controlled current, e.g., hopping conduction; space charge limited current (SCLC); Poole-Frenkel-effect (PFE).
- (2) Interface controlled current, e.g., thermionic (field) emission; tunneling carrier injection.

Moreover, the classification into (a) and (b) is very rudimentary, as in any MIM, at least, one mechanism from each class is working at the same current level in order to describe the steady-state leakage current. Undisturbed bulk properties cannot be assumed for thin film MIM structures because interface regions usually occupy larger area of the film thickness which affects bulk properties. A model combining both types of mechanism, thermionic field emission for carrier injection (and ejection), at the two MI interfaces and drift-diffusion current in the bulk, is suggested by Crowell, Beguwala, and Sze, (Crowell and Sze, 1966; Crowell and Beguwala, 1971). Table 3 gives the mathematical formulation of such mechanisms (Sze and Ng, 2007). Further, Table 4 illustrates some examples of corresponding conduction mechanism in MIM. Moreover, these mechanisms have been described in following sections.

Bulk-limited conduction

The bulk-limited conduction mechanisms (Choi *et al.*, 2009) include Poole-Frenkel emission, hopping conduction, ohmic conduction, space- charge-limited conduction (SCLC) and ionic conduction. The important parameters in these types of conduction

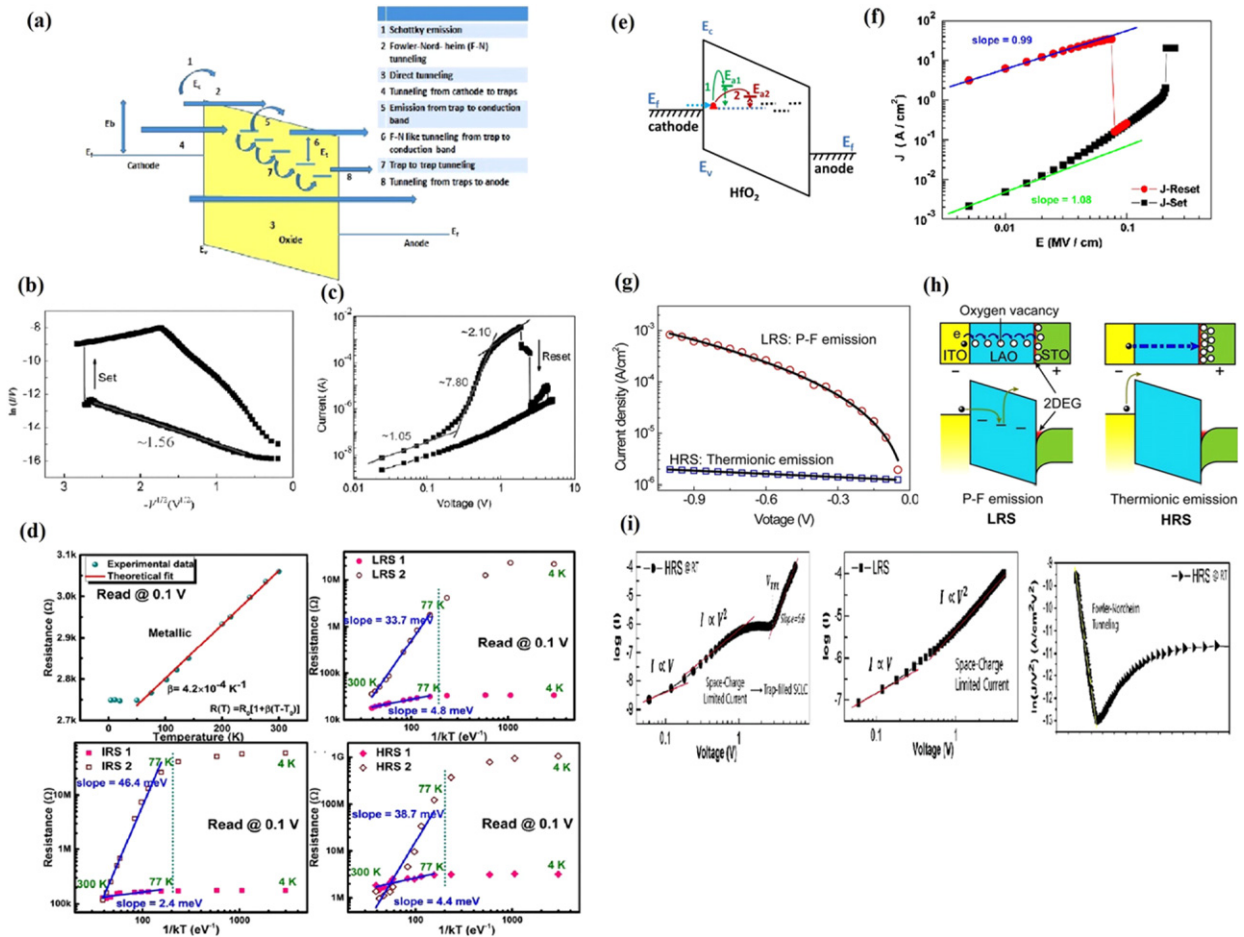


Fig. 4 (a) Conduction mechanism in MIM structure, (b) SCLC (c) and PF. Reproduced from Chen, C., Pan, F., Wang, Z.S., Yang, J., Zeng, F., 2012. "Bipolar resistive switching with self-rectifying effects in Al/ZnO/Si structure." *J. Appl. Phys.* 111 (1). (d) NNH and VRH. (e) NNH and VRH. Reproduced from Fang, R., Chen, W., Gao, L., Yu, W., Yu, S., 2015. "Low Temperature Characteristics of HfO_x - Based resistive random access memory." *IEEE Electron Device Lett.* 3106 (c), 1–3. (f) Ohmic and PF. Reproduced from Chang, W., Lai, Y., Wu, T., *et al.*, 2017. "Unipolar resistive switching characteristics of ZnO thin films for nonvolatile memory applications." *Appl. Phys. Lett.* 22110 (2008), 1–4. (g) PF and (h) thermionic emission. Reproduced from Wu, S., Ren, L., Qing, J., *et al.*, 2014. "Bipolar resistance switching in transparent ITO/LaAlO₃/SrTiO₃ memristors." *ACS Appl. Mater. Interfaces* 6, 8575–8579. (i) (I), (II) SCLC and (III) FN. Reproduced from Kim, A., Song, K., Kim, Y., Moon, J., 2011. "All solution-processed, fully transparent resistive memory devices." *ACS Appl. Mater. Interfaces* 3 (11), 4525–4530.

mechanisms are the trap energy level, trap spacing, trap density, electronic drift mobility, dielectric relaxation time, and density of states in the conduction band in the dielectric films.

Poole-frenkel emission

In the majority of literature, the identification of the Poole-Frenkel (PF) emission as the dominating current mechanism is investigated by the slope of line in the so-called PF plot ($\ln(J/E)$ vs. $E^{1/2}$), where J is current density, and E is applied electric field. However, such claims have to be checked critically as PF is applicable if the trap center is neutral with respect to captured carrier (electron, hole), because only then an attractive coulombic interaction will work as the charged carrier escapes from the then charged trap (Schroeder, 2015). Chen *et al.* have reported PF emission in Al/ZnO/Si based resistive switching (Chen *et al.*, 2012b). The conduction mechanisms (Chen *et al.*, 2012b) are explained by the PF and SCLC mechanisms for HRS and LRS, respectively, as illustrated in Fig. 4(b) and (c).

Hopping conduction

Hopping conduction is observed due to the tunneling effect of trapped electrons "hopping" from one trap site to another in dielectric films. Hopping conduction (Chiu *et al.*, 2009) depends on mean hopping distance, electron concentration in the conduction band of the dielectric medium, the frequency of thermal vibration of electrons at trap sites, and the activation energy. Fang *et al.* have reported nearest-neighboring hopping (NNH) and variable-range hopping (VRH) phenomena in HfO_x based resistive memory (Fang *et al.*, 2015), as illustrated in Fig. 4(d–e). Conduction mechanism in device shows a transition from the nearest-neighboring hopping to the variable range hopping below 77 K (Fang *et al.*, 2015).

Table 3 Various conduction mechanisms in MIM structure

Conduction mechanism	Current density expression	Voltage and temperature dependency
Fowler-Nordheim tunneling	$J \propto E_i \exp\left(-\frac{4\sqrt{2m^*}(q\Phi)^{3/2}}{3qhE_i}\right)$	$J \propto V^2 \exp\left(-\frac{b}{V}\right)$
Direct tunneling	$J \propto \exp\left(-\frac{4\sqrt{2qm^*}\Phi^{1/2}k}{3h}t_{OX}\right)$	$J \propto \exp(-bkt_{OX})$
Poole-Frenkel emission	$J \propto E_i \exp\left(-\frac{q(\Phi - \sqrt{qE_i/\pi\epsilon_i})}{kT}\right)$	$J \propto V \exp\left(q\left(2a\sqrt{\frac{V-\Phi}{kT}}\right)\right)$
Space-charge-limited conduction	$J = \frac{9\epsilon_i\mu V^2}{8d^3}$	$J \propto V^2$
Ionic conduction	$J \propto \frac{E_i}{T} \exp\left(-\frac{\Delta E_{ai}}{kT}\right)$	$J \propto V \exp\left(-\frac{b}{T}\right)$
Thermionic-field emission	$J = A^{**} T^2 \exp\left(-\frac{q(\Phi - \sqrt{qE_i/4\pi\epsilon_i})}{kT}\right)$	$J \propto T^2 \exp\left(q\left(a\sqrt{\frac{V-\Phi}{kT}}\right)\right)$
Schottky emission	$J = \frac{A}{A} \exp(\beta\sqrt{E/d})$	$J \propto T^2 e^{-b/T}$
Hopping	$J = qan(v) \exp\left(\frac{qaE - E_{ae}}{kT}\right)$	$\sim$
Ohmic	$J \propto E_i \exp\left(-\frac{\Delta E_{ae}}{kT}\right)$	$J \propto V \exp\left(-\frac{b}{T}\right)$

Source: J = Current density, V = Voltage applied, $\hbar$ = reduced Planck's constant, b = any constant, k = Boltzman constant, T = Temperature, t_{OX} = Oxide thickness, A^{**} = effective Richardson constant, Φ = barrier height, E_i = electric field in insulator, ϵ_i = insulator permittivity, m^* = effective mass, d = insulator thickness, ΔE_{ai} = activation energy of ions, a = mean hopping distance, n = electron concentration in the conduction band of the dielectric, (v) = frequency of thermal vibration of electrons at trap sites, and E_{ae} = activation energy of electrons.

Ohmic conduction

Although the energy band gap of dielectrics is, in general, large, yet thermal excitation may cause generation of a small number of current carriers. In ohmic conduction mechanism, a linear relationship exists between the current density and the electric field which is caused by the movement of such mobile electrons in the conduction band and holes in the valence band. Chang *et al.* have reported unipolar RS in Pt/ZnO/Pt with dominating conduction mechanisms in LRS and HRS to be ohmic behavior and PF emission, respectively (Chang *et al.*, 2017), as illustrated in Fig. 4(f).

Space-charge-limited conduction

Space-charge forces play a major role in the electrical properties of insulators as these solids normally have a relatively low density of free carriers so charge unbalance is easily produced by electric fields. There are two essential requisites to observe space-charge-limited currents of significant magnitude: (1) At least one of the two electrodes must form an ohmic contact with the insulator; (2) the insulator must be relatively free from trapping defects (Rose, 1955). Kim *et al.* have reported bipolar RS in indium tin oxide (ITO)/Ga-doped ZnO (GZO)/ITO (Kim *et al.*, 2011). The main conduction mechanism during the set process has been attributed to the trap-controlled space-charge limited conduction, and the resistance change has occurred by the modification of the potential barrier height because of the charge injection by Fowler-Nordheim tunneling (Kim *et al.*, 2011), as illustrated in Fig. 4(i(I-III)).

Electrode limited conduction

Primary electrode limited conduction mechanisms are Schottky emission, tunneling (Direct/Fowler-Nordheim) and thermionic-field emission as discussed in the following section.

Thermionic-field emission

Thermionic-field emission (TFE) is the thermally induced flow of charge carriers from a surface or over a potential-energy barrier. It happens because the thermal energy given to the charge carrier allows them to overcome the potential-energy barrier or work function of the material. Moreover, this theory is based on some assumptions (Sze and Ng, 2007): (1) Barrier height $\gg$ thermal energy (kT , where k is the Boltzmann's constant and T in temperature in 1K); (2) thermal equilibrium should exist at the plane that determines emissions; and (3) net current flow shall not affect this equilibrium. Due to such assumptions, the shape of the barrier profile becomes irrelevant and the current flow depends solely on the barrier height (Sze and Ng, 2007). Shuxiang *et al.* have reported bipolar RS in ITO/LaAlO₃(LAO)/SrTiO₃(STO) as illustrated in Fig. 4(g-h) with conduction in LRS, dominated by PF emission, which is related to electron hopping through the defect energy levels in the LAO film to the conduction band (Wu *et al.*, 2014). While for the HRS, the conduction behavior follows thermionic emission as the Schottky barrier in the LAO film is recovered because of return of VO's to the STO substrate under positive voltage (Wu *et al.*, 2014).

Schottky emission

Schottky emission in metal-semiconductor contacts involves the high-field emission of hot electrons from a metal into the conduction band of an insulator in contact with it. Schottky emission is temperature dependent and is favored over tunnel emission in thicker films and higher work functions (Emtage, 1962). Pan *et al.* have reported forming-free RS behavior in the Ru/Y₂O₃/Ta₂N memory device fabricated with full room temperature process (Pan *et al.*, 2011) with the dominant conduction mechanisms of low and high-resistance states to be ohmic conduction and Schottky emission, respectively (Pan *et al.*, 2011).

Table 4 Some examples of conduction mechanisms in MIM structure

Material	Conduction mechanism		
	LRS	HRS	
		Low Voltage	High Voltage
Al/ZnO/Si (Chen <i>et al.</i> , 2012b)	SCLC	PF	PF
Pt/HfO _x /TiN (Fang <i>et al.</i> , 2015)	NNH*, VRH**	NNH*, VRH**	NNH*, VRH**
Pt/ZnO/Pt (Chang <i>et al.</i> , 2017)	Ohmic	PF	PF
ITO/LAO/STO (Wu <i>et al.</i> , 2014)	PF	TFe	TFe
ITO/GZO/ITO (Kim <i>et al.</i> , 2011)	SCLC	SCLC	FN
TiN/HfO _x /Pt (Yu <i>et al.</i> , 2011)	PF	TAT	TAT

*At high T.

**At low T.

Table 5 Various applications and corresponding materials and references of RS

Form of Memristor	Broad area	Applications	Materials and references
Cross-bar array	Analog	Neuromorphic network	IGZO, (Wang <i>et al.</i> , 2012) ZnO, (Wang <i>et al.</i> , 2017) TiO ₂ (Prezioso <i>et al.</i> , 2015)
	Digital	Non-volatile memory	TaO _x , (Joshua Yang <i>et al.</i> , 2012) ZnO (Liu <i>et al.</i> , 2012)
		Hybrid memristor-CMOS	TiO ₂ (Cho <i>et al.</i> , 2015)
Discrete cells	Analog	Logic circuits	(Borghetti <i>et al.</i> , 2010; Chen <i>et al.</i> , 2016; Shaltoot and Madian, 2012)
		Oscillators	(Chen <i>et al.</i> , 2012b; Talukdar <i>et al.</i> , 2011; Kyriakides and Georgiou, 2015; Fouda and Radwan, 2014)
		Adaptive filters	(Driscoll <i>et al.</i> , 2010; Li and Chew, 2012)
		Chaotic system	(Itoh and Chua, 2008; Muthuswamy and Chua, 2010)

Tunneling

Tunneling is a quantum-mechanical phenomenon. The required conditions for tunneling are (Sze and Ng, 2007): (1) Occupied energy states and unoccupied energy states should exist at the same energy level on the opposite side of barriers; (2) the tunneling potential barrier height should be low, and the barrier width should be small; (3) the momentum is always conserved in the tunneling process. There exist different kinds of tunneling mechanisms.

Fowler-Nordheim (FN) tunneling is characterized by (1) the triangular shape barrier (Sze and Ng, 2007), and (2) tunneling to occur through only a part of the insulator layer. After tunneling through this triangular barrier, the rest of the insulator does not hinder the current flow. Direct tunneling is believed to occur below 5 nm, and for such a thin insulator, other quantum effects cannot be ignored (Sze and Ng, 2007). F-N tunneling is suggested by Kim *et al.* which influences charge injection to bring resistance change owing to the modification of the potential barrier height, as illustrated in Fig. 4(i(III)). Further, Shimeng Yu *et al.* have reported role of traps in tunneling for TiN/HfO_x/Pt as trap-assisted tunneling (TAT) (Yu *et al.*, 2011).

Applications

Memristive systems have been proposed for a wide range of applications such as programmable analog circuits, chaotic systems, nonvolatile memories, and neuromorphic systems etc. Some of these applications will be briefly discussed in this section. There are numerous applications of memristors as elaborated in Table 5 as discrete cells or in form of cross-bar. Applications of memristor can be in form of analog implementation or as digital or logical implementation as discussed below.

Analog Implementation

Memristor can be deployed for analog applications in the form of sinusoidal oscillators, programmable analog circuits, filters or commonly discussed in neuromorphic circuits.

Sinusoidal oscillators

The idea of memristor-based sinusoidal oscillators has been studied in a number of recent reports (Talukdar *et al.*, 2011; Kyriakides and Georgiou, 2015; Talukdar *et al.*, 2012; Takahashi *et al.*, 2017) by replacing some or all resistors and capacitors with memristors in the common oscillator circuits. Talukdar *et al.* (Talukdar *et al.*, 2011). have reported sustained oscillation and has obtained an approximated oscillation frequency. A relaxation oscillator is built using a memristor by substituting a capacitor in an equivalent

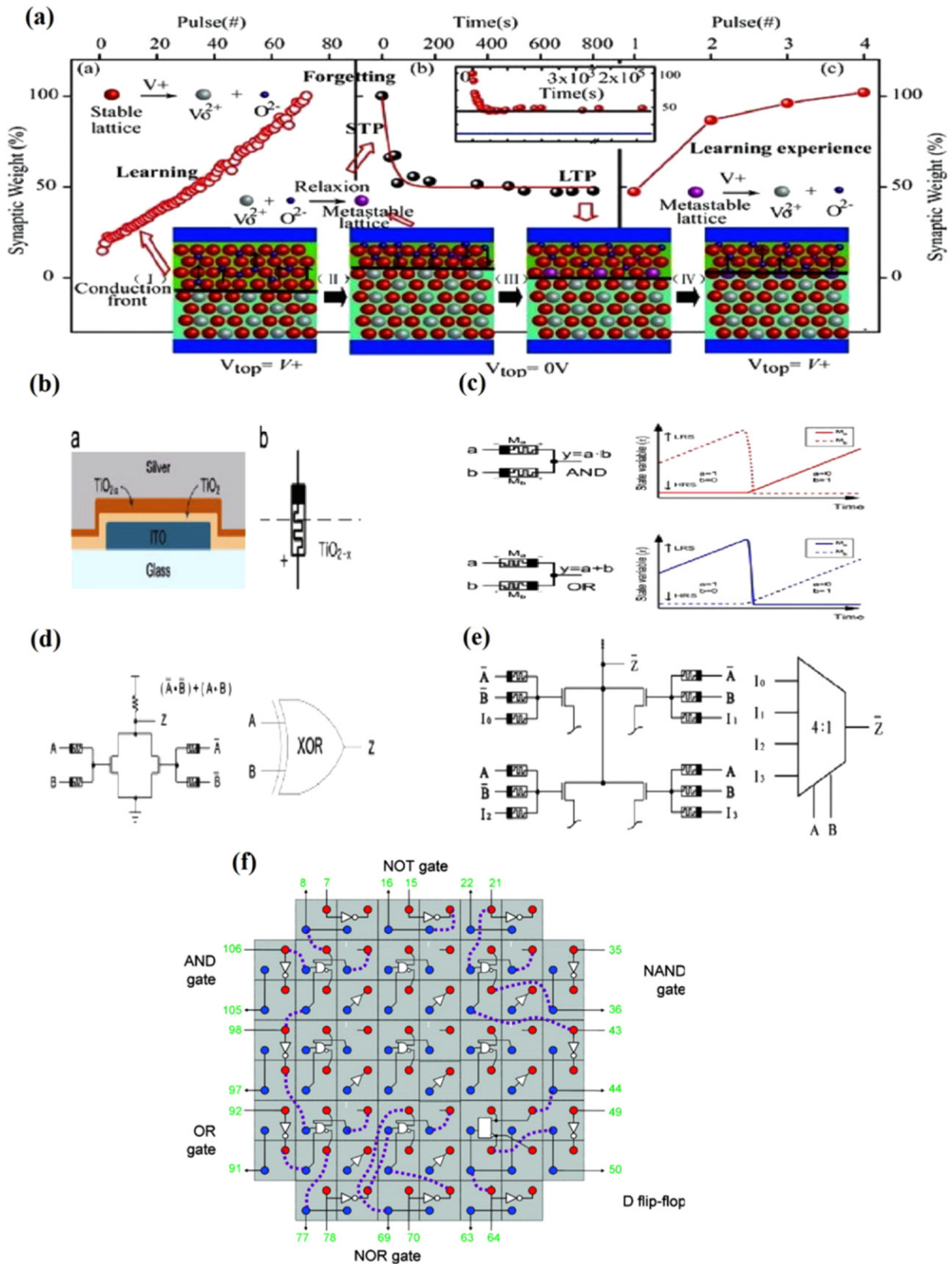


Fig. 5 (a) Conductance change in cycles and STP and LTP. Reproduced from Wang, Z.Q., Xu, H.Y., Li, X.H., *et al.*, 2012. "Synaptic learning and memory functions achieved using oxygen ion migration/diffusion in an amorphous InGaZnO memristor." *Adv. Funct. Mater.* 22 (13), 2759–2765. (b) Hybrid CMOS-Memristor, (c) AND and OR gate implementation through Hybrid CMOS-memristor. (d),(e) XOR and adder implementation. Reproduced from Cho, K., Lee, S., Eshraghian, K., 2015. "Memristor-CMOS logic and digital computational components." *Microelectron. J.* 46 (3), 214–220. (f) Several logic gates as implemented in Hybrid CMOS-Memristor. Reproduced from Xia, Q., Robinett, W., Cumbie, M.W., *et al.*, 2009. "Memristor-CMOS hybrid integrated circuits for reconfigurable logic." *Nano Lett.* 9 (10), 3640–3645.

Table 6 Various memory devices and performance parameters

Function	DRAM	SRAM	RRAM	Hard Disk	Flash
Non-volatility	no	No	yes	Yes	yes
Energy per bit (pJ)	0.005	0.0005	0.1–3	1–10 ¹⁰	0.00002
Program voltage	low	Low	low	High	high
Write/erase time	8–50 ns	1–8 ns	0.3–30 ns	10–30 ms	1–100 ms
Read time	50 ns	8 ns	20 ns	100 ns	50 ns
Multi-bit storage	no	No	yes	No	yes
Endurance	> 10 ¹⁶	> 10 ¹⁶	10 ¹²	> 10 ⁴	> 10 ⁴
Retention	< <second	till voltage applied	years	Years	years

Note: Reproduced from Zidan, M.A., Fahmy, H.A.H., Hussain, M.M., Salama, K.N., 2013. "Memristor-based memory: The sneak paths problem and solutions." *Microelectron. J.* 44 (2), 176–183.

resistor-capacitor (RC) oscillator (Kyriakides and Georgiou, 2015). Voltage-controlled memristor-based reactance-less oscillators are used with two different topologies which are resistor-memristor (R-M) and memristor-resistor (M-R) (Fouda and Radwan, 2014).

Programmable analog circuits

In many analog circuits such as amplifiers and filters, the programmable resistor with fine resolution are needed for adaptation to particular applications or for compensation of PVT (Process, Voltage, and Temperature) variations. In recent research works (Das and Singhal, 2014; Shin *et al.*, 2011; Pershin *et al.*, 2010; Wey and Jemison, 2010), many authors have used memristor as variable resistor to achieve such capabilities. Several other works have been published introducing different variable gain amplifier utilizing TiO₂ memristors (Das and Singhal, 2014; Shin *et al.*, 2011; Pershin *et al.*, 2010; Wey and Jemison, 2010). The memristor based potentiometer has the advantages of simple structure, small volume and continuous variable dynamic range (Tan *et al.*, 2017).

Adaptive filters and chaotic system

Adaptive filters based on memristor allows the gain and cut off frequency of the filter to be adjustable. Driscoll *et al.* (Driscoll *et al.*, 2010) have introduced the vanadium dioxide based memristive R_m LC band-pass adaptive filters. However, in an another memristor model based on ZnO nanowires, first- and second-order low-pass filter have been obtained (Li and Chew, 2012). Chaotic system is another area where memristors can be deployed. The most common application of chaotic systems is building secure communication systems. Chua has initiated memristor-based chaotic systems by modeling the memristor to produce a chaotic attractor with negative conductance and capacitor (Itoh and Chua, 2008). After this, Muthuswamy and Chua have extended this for chaotic oscillator where they have deployed an inductor-capacitor-memristor series circuit (Muthuswamy and Chua, 2010).

Neuromorphic circuits

A neuromorphic system is a hybrid analog-digital system mimicking neural architecture to pattern neurons by real-time computation, simulation, and hence emulating the nervous system. Williams *et al.* (Strukov *et al.*, 2008b) have proposed to emulate the synapse by memristor because of their comparable characteristics and since then many memristive systems have been fabricated using different materials (e.g., TiO_x (Prezioso *et al.*, 2016), Ag₂S (Hasegawa *et al.*, 2010), and InGaZnO (Wang *et al.*, 2012)). However, a complete equivalent of the biological synapse is difficult to achieve. Moreover, synaptic functions such as non-linear transmission characteristics, spike-rate dependent plasticity, spike-timing-dependent plasticity, long-term potentiation (LTP), short-term plasticity (STP) and "learning behavior (LB)" are achieved using a single synaptic device based on metal-insulator-metal (MIM) structure using different techniques (Zhang *et al.*, 2017a), as illustrated in Fig. 5(a) (Wang *et al.*, 2012).

Digital Applications

Memristors in general are sought for digital and logical applications. RRAM is most frequently pursued applications of memristor. Besides, a single memristor cell or a combination of cells in form of cross-bar may be sought for logical applications such as being implemented as AND, OR, or XOR gate etc.

Resistive random access memory

RRAM is a two-terminal device where the switching medium is sandwiched between top and bottom electrodes and the resistance of the switching medium can be modulated by applying electrical signal (current or voltage) to the electrodes. Before the physical evolution of the memristor, researchers have demonstrated high density memory applications of RS (Itoh and Chua, 2008; Muthuswamy and Chua, 2010; Xia *et al.*, 2009) where the insulating layer works as a storage medium. Though memristive characteristics were not realized, but the research works held memristor as a promising candidate to be used as non-volatile memory. Chen *et al.* (Talukdar *et al.*, 2012) have assumed Pt/Mg-ZnO/Pt device as a memristor and showed its RS characteristics which are reversible and steady, leading towards non-volatile memory. Recently, as a non-volatile memory the density of the memristor is

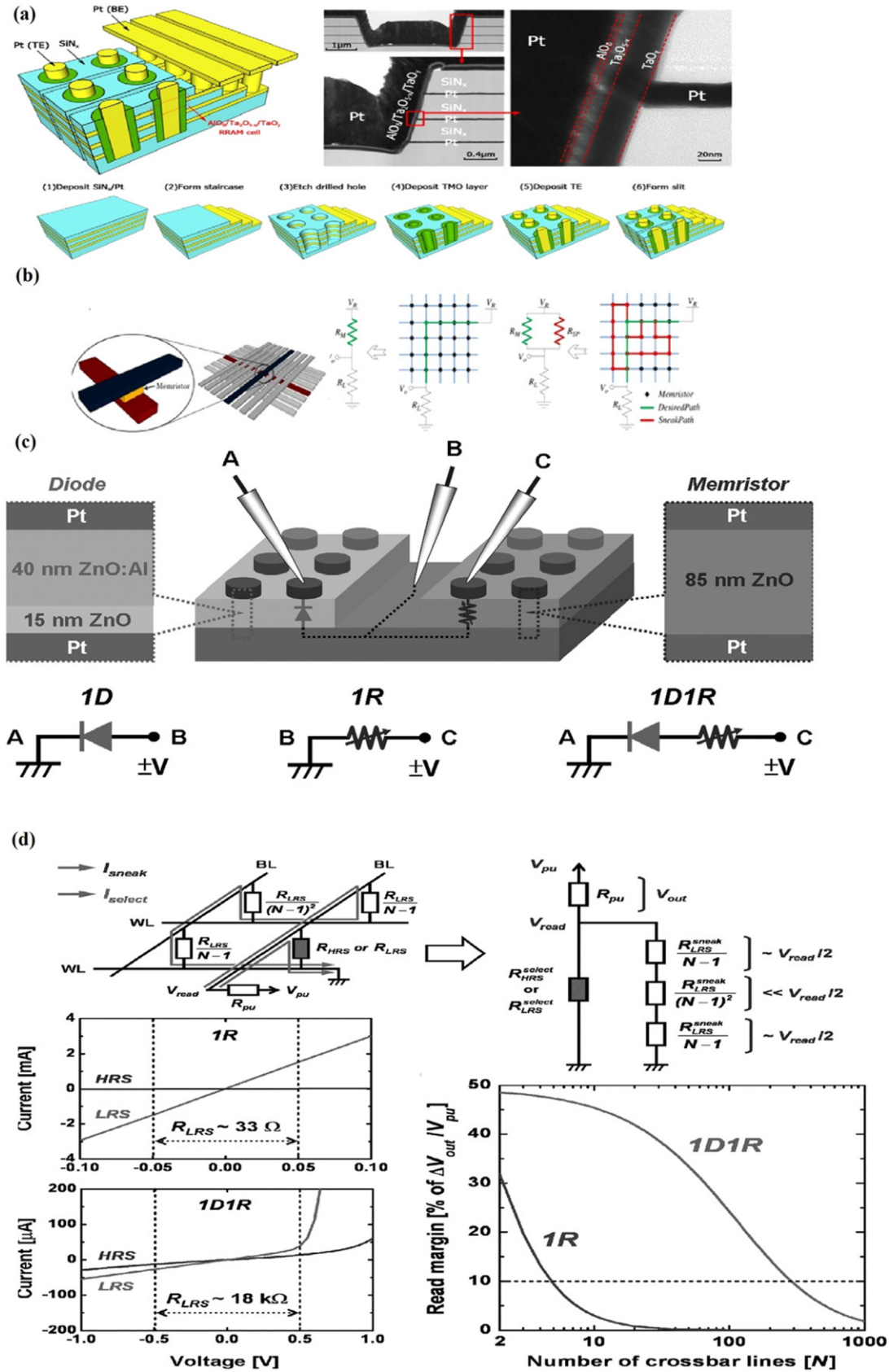


Fig. 6 (a) 3D RRAM. Reproduced from Bai, Y., Wu, H., Wu, R., *et al.*, 2014. "Study of multi-level characteristics for 3D vertical resistive switching memory." *Sci. Rep.* 1 (c), 1–7. (b) Sneak paths' issue in cross-bar. Reproduced from Zidan, M.A., Fahmy, H.A.H., Hussain, M.M., Salama, K.N., 2013. "Memristor-based memory: The sneak paths problem and solutions." *Microelectron. J.* 44 (2), 176–183. (c) 1D1R to solve crossbar issues, (d) 1D1R vs 1R. Reproduced from Liu, Z.J., Gan, J.Y., Yew, T.R., 2012. "ZnO-based one diode-one resistor device structure for crossbar memory applications." *Appl. Phys. Lett.* 100 (15).

reported to be 100 Gbits/cm² (Takahashi *et al.*, 2017), which requires very low energy as compared to the existing flash memory. Table 6 elaborates the comparative analysis of different memory technologies based on corresponding performance parameters.

Logic implementation

One major application of memristors is using them as the fundamental block of a logic gate. Borghetti *et al.* (Borghetti *et al.*, 2010) have realized all the fundamental Boolean operations using memristor based material implication logic. Imply (IMP) logic gate can be integrated into a crossbar array, and such integration can reduce power consumption and provides an opportunity for novel non-von Neumann architectures. Chen *et al.* (Chen *et al.*, 2016) have suggested a stateful OR logic operation which when operated in series with other logic operations (IMP, AND), only two voltages have to be changed while three voltages are necessary in the previous one-step OR logic operation. Shaltoot and Madian (Shaltoot and Madian, 2012) have introduced simplified carry look ahead adder based on IMPLY gate. In a CMOS- memristor hybrid circuit, it can be implemented as OR, AND or XOR gate, as shown in Fig. 5(b–f), (Cho *et al.*, 2015; Xia *et al.*, 2009).

Cross-Bar Architecture and Challenges

Crossbar array (Fig. 6(a)) architectures based on RRAMs can reduce memory cell size to $4F^2$ (F is minimum feature size), achieving high memory density (Yang *et al.*, 2013). Fig. 6(a) shows fabrication steps of 3D RRAM with TEM image of interfaces of one unit cell. Crossbar architecture allows three-dimensional (3D) stacking which increases memory density substantially. However, sneak-path current limits the number of cells in an array (Fig. 6(b)) as it creates crosstalk interference through neighboring cells which leads to misreading problems (Yang *et al.*, 2013). Researchers have proposed some solutions such as one diode-one resistor (1D1R) (Fig. 6(c)) (Zhang *et al.*, 2017b) for unipolar memory cells, and one selector-one resistor (1S1R) (Song *et al.*, 2017), and complementary resistive switches (CRSs) (Linn *et al.*, 2010) for bipolar memory cells to suppress crosstalk. 1D1R structure for devices showing unipolar behavior may tackle sneak-path issue, as illustrated in Fig. 6(c) and (d) (Liu *et al.*, 2012), by limiting the direction of current. ZnO-based 1D1R device consisting of a Pt/ZnO:Al/ZnO/Pt Schottky-type diode and a Pt/ZnO/Pt memristor using a room-temperature sputtering process exhibits stable switching for more than 10^3 cycles and good retention up to 10^4 s at 85°C, and desirable anti-crosstalk characteristics. Such designs show potential for integration in a crossbar memory array (Liu *et al.*, 2012), as shown in Fig. 6(d). The anti-crosstalk characteristics of 1D1R devices determine the maximum crossbar array size. The normalized read margin on the crossbar- line number (N) in 1R and 1D1R device decreases when increasing the crossbar-line number (N) for both 1R and 1D1R devices.

Challenges and Prospects

We sincerely thank entire research community around the world including scientists and engineers which has incessantly worked towards progress of research in this field. There are many challenges which still pose a lot of issues towards industrial implementations of device. Switching mechanisms of RRAMs are still debated. Filamentary or homogeneous mechanisms are although clearly stated in terms of work, but their clear demark is vague. Besides, cation migration mechanism as compared to anion migration mechanism may however be less popular theory but still is considered by many works. It poses the issue of demarking a clear boundary between two switching mechanisms. Cation migration in case of active electrodes such as Ag or Cu and with semiconductors like ZnO which is primarily dependent upon oxygen vacancy/ion migration creates a lot of confusion regarding their understanding. Repeatability of device is major issue which needs to be looked by any fabrication methods. Device property may vary from one method to another. Need is to look for a fabrication method which gives consistent properties of a device in terms of device performance. Besides, industrial implementation of RRAMs is dependent upon cross-bar fabrication limited by leakage current and other issues which require serious configuration changes in device structure, which is still very vague. Depending upon a device showing unipolar or bipolar switching, solution to cross-bar challenges changes which creates another twist in its implementation (Fouda and Radwan, 2014; Driscoll *et al.*, 2010; Biju *et al.*, 2011; Das *et al.*, 2018). Although 3D fabrication solution with many anomalies compensated by many solutions are there, but still very few companies have successfully implemented these in recent years.

Conclusion

In conclusion, we have observed fabrication, conduction mechanisms and applications of major oxide based memristors. DIBS has emerged as a suitable sputtering technique to fabricate oxide based memristors with consistent performance parameters. Major conduction mechanisms of memristors involve migration of vacancy/ion, or formation/annihilation of conducting paths. Among the applications, being explored in recent years, besides being used as memory cells neuromorphic applications of memristor as synapse is very promising. Many challenges are still there in design issues of RRAMs in terms of consistent performance parameters of device to use it for practical implementations. We hope our work would help the research community to investigate further studies in field of resistive switching.

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Introduction: New Research Trends in Magnetism and Magnetic Technologies

Manh-Huong Phan, Department of Physics, University of South Florida, Tampa, FL, United States

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Magnetic materials are key components in many electronic devices, whose applications range from electric transformers to computer hard-disk drives, mobile phones, sensors, motors, generators, refrigerators, medical devices, and home appliances. The majority of the research on magnetic materials focuses on the engineering of magnetic properties and the discovery of new materials with desirable characteristics for use in next-generation devices. This volume consists of thirteen chapters that feature the most topical research areas in magnetism.

Correlated electron magnetic oxides, such as $R_{1-x}A_xMO_3$, where $R = \text{La, Nd, Pr, etc.}$, $A = \text{Ca, Sr, Ba, etc.}$, and $M = \text{Mn, Co, and Fe}$, exhibit rich complexity in their fundamental physical properties due to the intricate interplay between structural, electronic, and magnetic degrees of freedom. A variety of novel phenomena such as the magnetoresistive effect (MRE), magnetoelectric effect (MEE), electrocaloric effect (ECE), magnetocaloric effect (MCE), spin Seebeck effect (SSE), and spin Hall magnetoresistance (SMR) have been discovered in these systems. Understanding the ground state magnetic properties of these systems allows for not only manipulating such novel effects towards device applications but also forms the foundation for exploring new functionalities in emergent materials that exhibit noncollinear spin textures and skyrmion properties. Chapter (Kozlenko, Phan, Dang) introduces the underlying physics of manganites. It discusses the microscopic mechanisms that determine the magnetic and associated physical properties of these oxides under high pressures, based on several important findings including neutron diffraction studies. It also shows how the magnetic functionality of a material can be manipulated by external stimuli for technological applications.

Exploring the magnetic field response of a magnetic material, based on the MCE, has driven solid-state magnetic cooling technology. This new technology has the potential to replace conventional gas compression/expansion-based cooling techniques, due to its high energy efficiency, compactness, and environmental friendliness. To fully exploit this phenomenon, however, technical challenges regarding the optimization of magnetocaloric functionalities and magnetic refrigeration must be resolved. Chapter (Moreno-Ramírez, Law, Díaz-García, Franco) reviews the most remarkable developments in magnetocaloric materials for cryogenic or room temperature cooling applications. It highlights the importance of the thermomagnetic phase transitions where the MCEs are largest, material optimization routes, and analysis methods to properly determine the magnetocaloric parameters of the materials. New research trends in this field are also outlined.

Exploring the electric field response of a material, also known as a multiferroic system that exhibits a large MEE, has been a subject of extensive research, which has driven the field of multiferroics towards realizing high-energy-efficiency scalable memory and logic operations for a next generation of computing devices. Chapter (Xu, Binex) assesses the current understanding of the magnetoelectric coupling mechanisms in multiferroic systems. The focus lies in the design of materials that exhibit enhanced magnetoelectric couplings. It is anticipated that the future research in magnetoelectric materials will be driven by emergent applications in memory, sensing, and antennas. There is a current need for developing energy-efficient and ultrafast complementary metal-oxide-semiconductor (CMOS) devices, which will facilitate further research and continue to drive this active research field.

Soft ferromagnetic (FM) microwires with novel properties including the giant magnetoimpedance (GMI) effect continue to have important impacts on the development of ultrasensitive magnetic sensors that have applications in nearly all sectors. Different types of GMI based sensors have been developed and commercialized. Current efforts are devoted to improving the magnetic properties and GMI effect in a wide range of Co-rich and FINEMET-based microwires through heat treatment and other techniques. Chapter (Zhukov, Ipatov, Corte-Leon, Blanco, Zhukova) introduces novel routes that allows for the development of low-cost magnetic microwires for sensor applications. It shows how the GMI effect obtained in amorphous Co-rich microwires can be further improved by appropriate annealing, including conventional annealing, stress annealing, and Joule heating. It also shows that magnetic softening and the GMI effect can be significantly improved in Fe-rich microwires upon nanocrystallization. A combination of conventional and stress annealing can drastically improve the GMI effect in these microwires, making them a competitive candidate for magnetic sensing applications.

In addition to soft magnetic microwires' existing applications, incorporating them into a polymer matrix or arranging them in a specular configuration has opened new opportunities for creating new composite materials with novel functionalities and applications that would be otherwise absent in single microwires. For instance, a new concept of incorporating Co-rich microwires with an optimized GMI effect into fiber-reinforced composites as means of sensing stress and external magnetic fields through changes in impedance, which potentially offers an alternative to optical fibers for self-monitoring composites. The inclusion of these microwires with superior sensing characteristics can also lead to an enhancement in the structural integrity of the composites. A versatile metacomposite enabled by such magnetic microwires has recently been engineered. Chapter (Estevez, Qin) discusses several optimization strategies of microwire metacomposites based on microstructural parameters, in-built vertical interfaces, hybridization, and external stimuli. It provides a thorough analysis of the manufacturing process of microwire metacomposites and their unparalleled advantages in microwave sensing and cloaking areas. New strategies for improving the functionalities of microwire metacomposites for multifunctional applications are also proposed in this chapter.

Along with soft magnetic materials, hard magnetic materials (also known as permanent magnetic materials) have found many important applications in industries and home appliances. The design and manufacturing of hard magnetic materials with enhanced

saturation magnetization and coercivity (large maximum energy product) that are thermally stable at high temperatures remains a challenging task. Nanostructuring of such materials may provide an alternative approach for improving the hard magnetic properties, since their dimensions are of the order of the domain wall width, which is the dimension defining length scale of magnetization processes. Chapter (*Nam, Hai, Luong*) presents an overview of the recent developments in rare-earth- and rare-earth-free hard magnetic nanostructured materials, with an in-depth analysis of their magnetic properties and perspective applications.

Among magnetic materials being explored for spintronics, iron garnets are an emerging candidate, owing to their insulating, ferrimagnetic (FiM) characteristics, ultralow Gilbert damping (as low as 10^{-5}), strong magneto-optical response, and tunable magnetic anisotropy. Research has shown that the magnetic properties of iron garnets depend on rare-earth substitution, magnetoelastic or growth-induced anisotropy, film thickness, and stoichiometry. There is a high demand for growing high quality garnet films for exploiting magnonic and spintronic effects like spin wave propagation, the spin Hall effect, SSE, spin-orbit torques, or spin wave computing. Chapter (*Holzmann, Albrecht*) assesses the most recent advances in garnet film growth. Novel strategies for growing garnet films with tunable magnetic anisotropy are discussed. A wide range of applications offered by such films is also highlighted.

Unlike FM or FiM materials, antiferromagnets (AFMs) with zero net magnetic moment have historically been thought of as interesting but useless materials. However, recent study has shown that AFMs are a very promising candidate for use in modern spintronic devices. Among many advantages AFMs offer, these materials carry zero stray fields and possess high spin precession frequency in the terahertz range, making them a highly competitive candidate for ultrafast spintronics. Chapter (*Kalappattil*) provides a state-of-the-art understanding of AFM-based spintronics and its future perspectives. Although the development of AFM-based devices is in its infancy, AFM spintronics appears to be important for neuromorphic and quantum computing applications.

Spin orbit torque (SOT) provides a novel platform for the electrical manipulation of magnetization in spintronic devices - the key components in computing systems. Chapter (*Hung, Chanda, Srikanth, Phan*) discusses basic concepts, recent progresses, and future perspectives for SOT-based devices. It assesses a wide variety of SOT materials, showing a new and promising perspective for SOT devices based on two-dimensional (2D) van der Waals materials and heterostructures.

Magnetic tunnel junctions (MTJs) also play a key role in such spintronic devices. The performance of these junctions is defined by a tunneling magnetoresistance ratio and a resistance area product. These performance indicators have been improving over the last decades. Chapter (*Hirohata*) provides a critical review of recent studies and spin-dependent tunneling phenomena. It shows how MTJs can be efficiently switched by SOT by integrating a material with large spin-orbit interaction. Insertion of a 2D material can improve the interfacial quality of the overall MTJ structure to reduce unwanted spin scattering. Such MTJs can find important applications in magnetic sensing and neuromorphic computing.

In the field of spin caloritronics, the interconversion between spin, charge, and heat currents has been actively investigated from the viewpoints of fundamental physics and thermal energy engineering. Chapter (*Uchida*) summarizes basic behaviors, spin-charge-heat current conversion symmetries, and functionalities of spin-caloritronic phenomena and provides directions on future studies in this active field.

Unlike FM, FiM, and AFM materials, helimagnetic materials have emerged as a novel class of magnetic materials for modern spintronics. Chapter (*Mandrus*) reviews the basic properties of Yoshimori-type and Dzyaloshinskii-type helimagnets, followed by a discussion of several electronic functionalities of recently discovered helimagnets. These include some interesting properties of CrNb_3S_6 - a monoaxial chiral helimagnet that exhibits magnetically tunable periodicity, 1D magnetic solitons, and a huge electrical magnetochiral effect. The ability of helimagnets to create miniature inductors and the possibility of controlling the handedness of helimagnets to encode information are also discussed in this chapter.

Finally, Chapter (*Sheka*) assesses the recent developments and current challenges in theory, fabrication, and characterization of curvilinear magnetic nanostructures, which is also known as curvilinear magnetism. It shows how geometrical effects can mediate magnetic interactions resulting in new functionalities in curved magnetic wires and thin films. The chapter closes with discussions on new research directions and perspective applications of curvilinear magnetism.

Spin Caloritronics

Ken-ichi Uchida, National Institute for Materials Science, Tsukuba, Ibaraki, Japan

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Abstract

In the field of spin caloritronics, the interconversion between spin, charge, and heat currents has been actively investigated from the viewpoints of fundamental physics and thermal energy engineering. This article summarizes basic behaviors, spin-charge-heat current conversion symmetries, and functionalities of spin-caloritronic phenomena and provides directions on future studies in this field.

Nomenclature

AMPE	anisotropic magneto-Peltier effect
AMSE	anisotropic magneto-Seebeck effect
AEE	anomalous Ettingshausen effect
ANE	anomalous Nernst effect
ISHE	inverse spin Hall effect
LIT	lock-in thermography
SHE	spin Hall effect
SPE	spin Peltier effect
SSE	spin Seebeck effect
YIG	yttrium iron garnet or $\text{Y}_3\text{Fe}_5\text{O}_{12}$
θ_{H}	angle between magnetic field and $+x$ direction
θ_{M}	angle between magnetization and charge/heat current
Π_{AEE}	anomalous Ettingshausen coefficient
S_{ANE}	anomalous Nernst coefficient
J_{c}	charge current
j_{c}	charge current density
$j_{\text{c,ANE}}$	charge current density driven by anomalous Nernst effect
ρ	charge density
$L_{11}, L_{12}, L_{21}, L_{22}$	components of transport coefficient matrix in Eq. (6).
$M_{11}, M_{12}, M_{13}, M_{21}, M_{22}, M_{23}, M_{31}, M_{32}, M_{33}$	components of transport coefficient matrix in Eq. (7).
$\rho_{xx} (\rho_{xy})$	diagonal (off-diagonal) component of electrical resistivity tensor
$\alpha_{xx} (\alpha_{xy})$	diagonal (off-diagonal) component of thermoelectric conductivity tensor
H_{eff}	effective magnetic field
∇V	electric field
σ	electrical conductivity
$\sigma_{\uparrow} (\sigma_{\downarrow})$	electrical conductivity for up-spin (down-spin) electrons
$\rho_{\parallel} (\rho_{\perp})$	electrical resistivity when magnetization is parallel (perpendicular) to charge current
μ	electrochemical potential
$\mu_{\uparrow} (\mu_{\downarrow})$	electrochemical potential for up-spin (down-spin) electrons
$-e$ ($e > 0$)	electron charge
$\hbar/2$	electron spin angular momentum
α	Gilbert damping constant
γ	gyromagnetic ratio
Q	heat
J_{q}	heat current
$j_{\text{q,AEE}}$	heat current density driven by anomalous Ettingshausen effect
L_x, L_y, L_z	lengths along x , y , and z directions
A_{AMPE}	lock-in amplitude of temperature modulation induced by anisotropic magneto-Peltier effect
A_{AEE}	lock-in amplitude of temperature modulation induced by anomalous Ettingshausen effect
ϕ_{AMPE}	lock-in phase of temperature modulation induced by anisotropic magneto-Peltier effect
ϕ_{AEE}	lock-in phase of temperature modulation induced by anomalous Ettingshausen effect
H	magnetic field
$\mathbf{m}$	magnetic moment or unit vector along magnetization
M	magnetization
J_{c}	magnitude of charge current
j_{c}	magnitude of charge current density

H	magnitude of magnetic field
$\mathbf{n}$	normal vector of magnetic material/conductor junction interface
Π	Peltier coefficient
M_s	saturation magnetization
S	Seebeck coefficient
$S_{\parallel} (S_{\perp})$	Seebeck coefficient when magnetization is parallel (perpendicular) to charge current
$\mathbf{j}_s$	spin current or spatial direction of spin current
j_s	spin current density
$\mathbf{s}$	spin polarization vector
T	spin relaxation term
T	temperature
ΔT_{SPE}	temperature change induced by spin Peltier effect
ΔT	temperature difference
∇T	temperature gradient
∇T_{NiFe}	temperature gradient in $\text{Ni}_{81}\text{Fe}_{19}$
∇T_{YIG}	temperature gradient in $\text{Y}_3\text{Fe}_5\text{O}_{12}$
ΔT_{AMPE}	temperature modulation induced by anisotropic magneto-Peltier effect
ΔT_{AEE}	temperature modulation induced by anomalous Ettingshausen effect
$\kappa_P (\kappa_{\text{AP}})$	thermal conductivity for parallel (antiparallel) magnetization configuration
η_{TE}	Thomson-effect-induced temperature modulation normalized by charge current density and temperature gradient
t	time
$J_{\uparrow} (J_{\downarrow})$	up-spin (down-spin) electron flow
μ_0	vacuum permeability
ΔV	voltage difference
k	wavenumber

Key Points

- Spin caloritronics is a research field based on the interdisciplinary fusion between spintronics, thermoelectric, and thermal energy engineering.
- In spin caloritronics, a wide variety of thermo-spin, magneto-thermoelectric, and thermomagnetic effects have been investigated from the viewpoints of fundamental physics and thermal energy engineering.
- This article summarizes basic behaviors, spin-charge-heat current conversion symmetries, and functionalities of spin-caloritronic phenomena.

Introduction

The field of spintronics presents great potential for next-generation electronic technologies, in which electron spins are actively exploited as new information and energy carriers in addition to electron charges (Maekawa *et al.*, 2017). Spintronics has effectively contributed to important scientific discoveries and industrial applications, e.g., read heads in hard disk drives, magnetoresistive sensors, and magnetic random-access memories (Hirohata *et al.*, 2020). A key factor in spintronics is a spin current, i.e., a pure flow of spin angular momentum without an accompanying charge current. Spin currents are used to write and read information in spintronic devices. Moreover, its concept has helped discover various spin-dependent and spin-driven transport phenomena. Principles and techniques to generate, detect, and control spin currents are being rapidly developed since the beginning of the 21st century.

The interplay between spin, charge, and heat currents has been extensively investigated. Spin caloritronics is a research field that comprises spintronics, thermoelectric, and thermal energy engineering (Bauer *et al.*, 2012; Boona *et al.*, 2014; Uchida, 2021). This field was originated from the theoretical study by Johnson and Silsbee (Johnson and Silsbee, 1987), who established the non-equilibrium thermodynamics of the spin–charge–heat interaction in metal-based magnetic heterostructures. After several decades, Hatami *et al.* theoretically predicted that the magnetization direction of a ferromagnet can be reversed using a spin-polarized heat current and introduced the term “spin caloritronics” (Hatami *et al.*, 2007). One of the reasons for the rapid development of spin caloritronics is the discovery of the spin Seebeck effect (SSE), which refers to the generation of spin currents caused by heat currents in a magnetic material (Uchida *et al.*, 2008; Uchida *et al.*, 2010a,b; Jaworski *et al.*, 2010). To clarify the mechanism of SSE, many condensed matter physicists have started to study spin caloritronics. Nowadays, spin caloritronics has grown into an

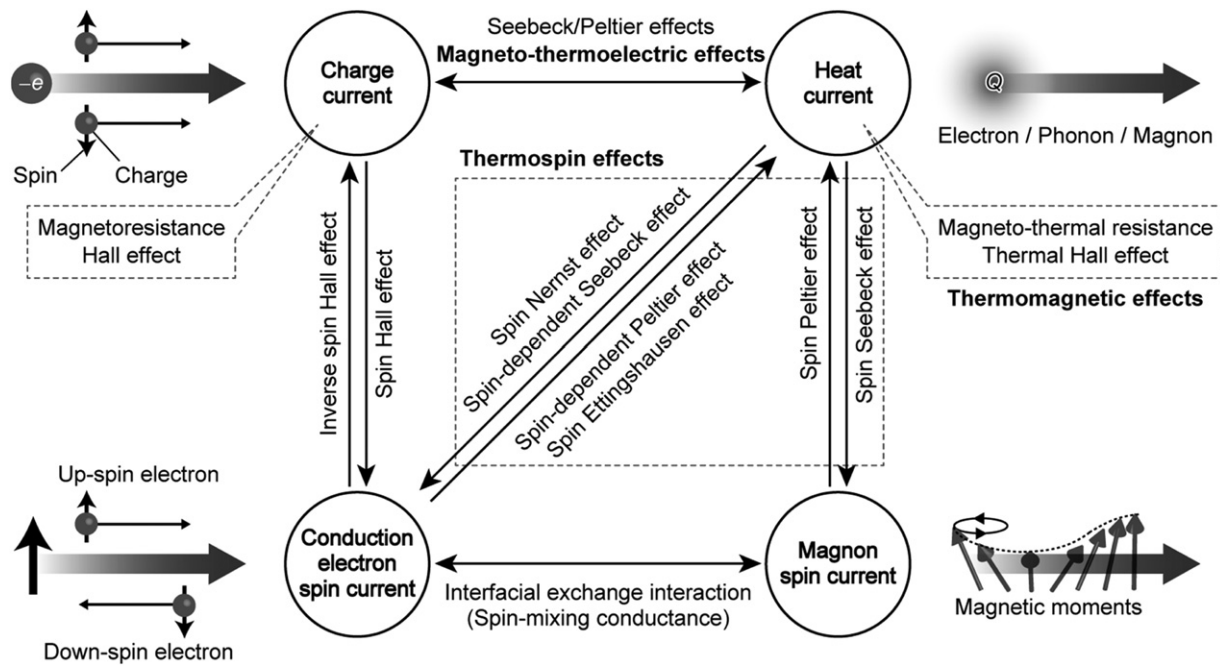


Fig. 1 Conversion phenomena between charge, heat, conduction electron spin, and magnon spin currents. $-e$ and Q denote the electron charge and heat, respectively.

interdisciplinary field worldwide. Since the discovery of SSE, various novel thermo-spin conversion principles have been derived, and unconventional thermoelectric functionalities based on spin caloritronics have been demonstrated.

This article is organized as follows: “Fundamentals” classifies spin-caloritronic phenomena and introduces the concept of spin currents. “Transport Phenomena in Spin Caloritronics” reviews the basic properties of spin-caloritronic phenomena and shows our representative experimental results. “Future Directions” discusses a future direction for spin caloritronics. “Conclusions” provides the conclusion. We expect that this article will further invigorate basic science and application studies on spin caloritronics and accelerate new entry into this field from various research areas.

Fundamentals

Classification of Spin-Caloritronic Phenomena

In spin caloritronics, various transport phenomena based on the interplay between the spin, charge, and heat currents have been discovered. The terminologies of spin-caloritronic phenomena are often confusing because of their similarities. Thus, we classified spin-caloritronic phenomena into three categories: (1) thermo-spin effect, (2) magneto-thermoelectric effect, and (3) thermomagnetic effect (Fig. 1). The thermo-spin effect refers to the conversion between spin and heat currents. Since the discovery of SSE, various thermo-spin effects have been investigated in magnetic materials and their junction structures because spin currents are carried not only by conduction electrons but also by the collective dynamics of local magnetic moments, i.e., spin waves or magnons. The magneto-thermoelectric effect refers to the conversion between charge and heat currents in a conductor under a magnetic field or in a magnetic material with spontaneous magnetization, where thermoelectric conversion properties depend on the magnetic field or magnetization. Magneto-thermoelectric effects are different from thermo-spin effects irrespective of their similar thermoelectric conversion symmetries and functionalities. The thermomagnetic effect represents a phenomenon in which heat transport, i.e., thermal conductivity, depends on the magnetic field or magnetization. In addition to this classification, thermo-spin, magneto-thermoelectric, and thermomagnetic effects have been further categorized into longitudinal and transverse effects, in which the output current is generated parallel and perpendicular to the input current, respectively. Fig. 2 shows the longitudinal and transverse magneto-thermoelectric/thermomagnetic effects. Each spin-caloritronic phenomenon will be discussed in detail.

Definition of Spin Currents

Before introducing the basic behaviors of spin-caloritronic phenomena, we review the definition of a spin current by comparing it with the definition of a charge current (Maekawa et al., 2017). The charge current density (j_c) is defined by the continuity equation of the charge density (ρ) as

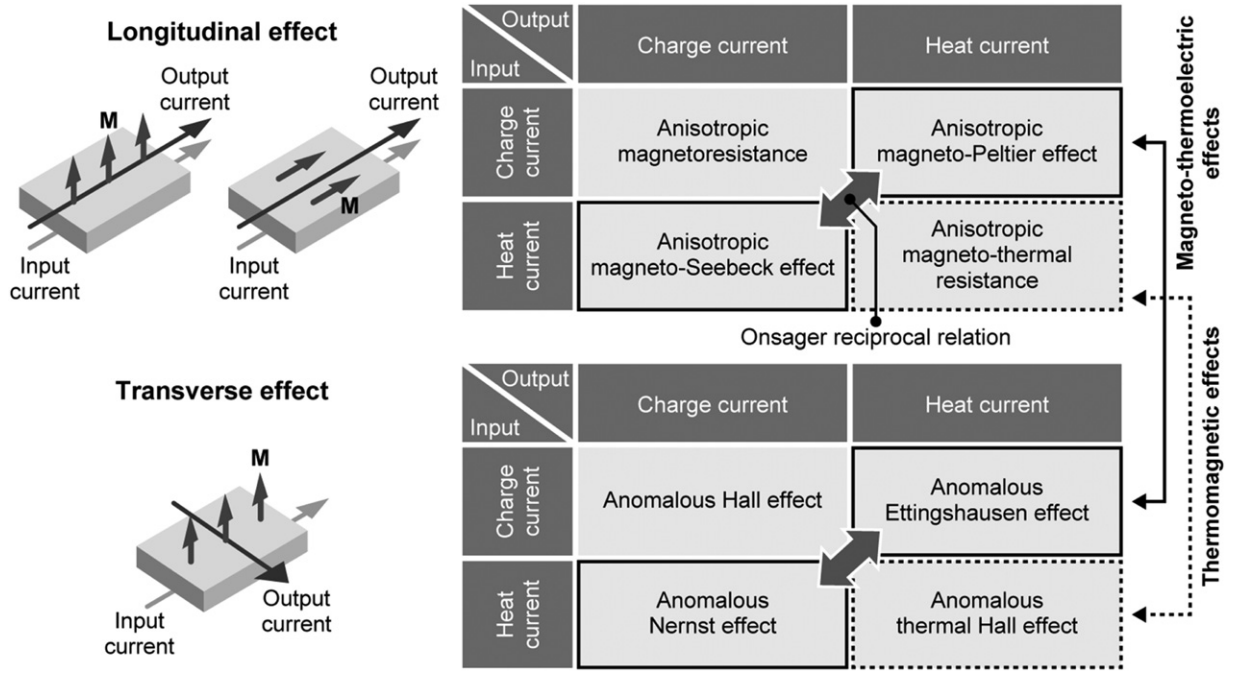


Fig. 2 Magneto-thermoelectric and thermomagnetic effects in magnetic materials. $\mathbf{M}$ denotes the magnetization vector.

$$\frac{d\rho}{dt} = -\nabla \cdot \mathbf{j}_c, \quad (1)$$

where t denotes time. This equation expresses the conservation of the electron charge. Similarly, the spin current density ($\mathbf{j}_s$) is defined by the continuity equation of the magnetization ($\mathbf{M}$) as

$$\frac{d\mathbf{M}}{dt} = -\gamma \nabla \cdot \mathbf{j}_s + \mathbf{T}. \quad (2)$$

This equation expresses the conservation of the angular momentum. Here, γ is the gyromagnetic ratio and $\mathbf{M}$ includes not only the macroscopic spontaneous magnetization but also nonequilibrium components. Eqs. (1) and (2) indicate that a spin current transports magnetic moments or angular momentum, whereas a charge current transports electron charge. In contrast to the charge current, which is a conserved flow, the spin angular momentum dissipates into, for example, the lattice system; the spin current is a non-conserved flow that disappears within a certain distance and time. Thus, the right-hand side of Eq. (2) includes the spin relaxation term $\mathbf{T}$. On a sufficiently short length scale for the spin relaxation to be negligible, the spin current can be approximated as a conserved flow. Therefore, spin current physics has rapidly progressed with the development of nanotechnology, which enables the production of devices that are smaller than the spin relaxation length. The spin current is a second-order tensor quantity with two degrees of freedom, i.e., the spatial direction in which the spin current flows and the spin polarization direction. However, the spin current can be treated as a vector quantity when the quantization axis of spins is fixed (the operator ∇ on the right-hand side of Eq. (2) acts on the spatial component). The spin current can be carried by conduction carriers with spin angular momenta, e.g., conduction electrons, magnons or spin waves, and spinons, and can exist in edge (surface) states in 2D (3D) topological insulators. Hereafter, we focus on spin current transport phenomena driven by conduction electrons and magnons because they are the central foci of spin caloritronics.

Conduction electron spin current

When an external force, such as an electric field, is applied to electrical conductors, a non-equilibrium charge current is driven by conduction electrons. Similarly, spins can be carried by conduction electrons, and the conduction electron spin current exists only in electrical conductors. Assuming that the spin quantization axis is fixed, the charge current ($\mathbf{J}_c$) and conduction electron spin current ($\mathbf{J}_s$) can be expressed as follows:

$$\mathbf{J}_c = e(\mathbf{J}_\uparrow + \mathbf{J}_\downarrow), \quad (3)$$

$$\mathbf{J}_s = \frac{\hbar}{2}(\mathbf{J}_\uparrow - \mathbf{J}_\downarrow), \quad (4)$$

where $\mathbf{J}_\uparrow$ ($\mathbf{J}_\downarrow$) is the up-spin (down-spin) electron flow, $-e$ ($e > 0$) is the electron charge, and $\hbar/2$ is the electron spin angular momentum. The conduction electron spin current is often expressed as the same unit as the charge current by multiplying Eq. (4) by $2e/\hbar$. When the magnitude of $\mathbf{J}_\uparrow$ is different from that of $\mathbf{J}_\downarrow$, the conduction electron spin current becomes finite. In ferromagnetic metals, in which conduction electrons are spin-polarized, the charge current is always accompanied by a spin current;

i.e., $J_c \neq 0$ indicates $J_s \neq 0$. An important case is that the up- and down-spin electron flows have the same magnitude but opposite directions to each other, as depicted in the bottom-left image of Fig. 1. This leads to the generation of a pure spin current without any charge current; i.e., $J_c = 0$ and $J_s \neq 0$. A pure spin current plays a key role in various spin-transport phenomena and spintronic applications. The conduction electron spin current can be injected into a nonmagnetic material using various methods, e.g., nonlocal spin-injection techniques (Jedema *et al.*, 2001; Kimura *et al.*, 2007) and the spin Hall effect (SHE) (Valenzuela and Tinkham, 2006; Kimura *et al.*, 2007; Sinova *et al.*, 2015). The propagation length of the conduction electron spin current is known as the spin diffusion length (Bass and Pratt, 2007), which is in the order of several nanometers in metals with strong spin-orbit interactions, e.g., Pt. In contrast, the spin diffusion length can reach several hundreds of nanometers or several micrometers in conductors with weak spin-orbit interactions. Using the latest microfabrication technologies and thin-film deposition methods, vertical and lateral magnetic heterostructures that are smaller than the spin diffusion length can be easily fabricated. Thus, the physics and behavior of the conduction electron spin current have been investigated in detail.

Magnon spin current

A magnon is a quasiparticle of a spin wave, which is the collective dynamics of localized magnetic moments in magnetic materials. The magnon spin current is the flow of the spin angular momentum carried by magnons (the bottom-right image of Fig. 1). A magnon spin current can exist even in magnetic insulators without conduction electrons and is a pure spin current because magnons have no charge. Magnons follow Bose-Einstein statistics and are thermally excited in magnetic materials at finite temperatures. However, the net flow of spin angular momentum carried by magnons, i.e., the magnon spin current, is not generated under thermal equilibrium conditions because magnons with wavenumbers $\mathbf{k}$ and $-\mathbf{k}$ exist in equal numbers. The magnon spin current is generated when there is an imbalance in the numbers of $\mathbf{k}$ and $-\mathbf{k}$ magnons caused by external forces. The magnon dynamics can be obtained by solving the Landau-Lifshitz-Gilbert equation, which is the equation of motion for the magnetic moment:

$$\frac{d\mathbf{m}}{dt} = -\gamma \mathbf{m} \times \mathbf{H}_{\text{eff}} + \frac{\alpha}{M_s} \mathbf{m} \times \frac{d\mathbf{m}}{dt}. \quad (5)$$

Here, $\mathbf{H}_{\text{eff}}$ is the effective magnetic field, which includes the contributions of the external magnetic field, exchange interaction, magnetic dipole interaction, and magnetic anisotropy; M_s is the saturation magnetization; and α is the Gilbert damping constant. The first term in Eq. (5) defines the precession motion of $\mathbf{m}$ around the $\mathbf{H}_{\text{eff}}$ direction, which can be derived from the Heisenberg equation of motion. The second term is the relaxation term phenomenologically introduced to direct $\mathbf{m}$ in the $\mathbf{H}_{\text{eff}}$ direction. Due to Gilbert damping, the magnon spin current is also a non-conserved quantity. However, the propagation length of the magnon spin current can reach the order of micrometers or millimeters in materials with small α values, e.g., yttrium iron garnet $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG), which is significantly longer than the spin diffusion length of the conduction electron spin current (Kajiwaru *et al.*, 2010). The magnon spin current can be generated by nonlocal spin injection (Cornelissen *et al.*, 2015), microwave-driven spin pumping (Kajiwaru *et al.*, 2010), and temperature-gradient-driven SSE (Uchida *et al.*, 2010a,b).

The magnon spin current in a magnetic material and the conduction electron spin current in a metal can be interconverted via the interfacial exchange interaction at the magnetic material/metal junction, which is known as spin-mixing conductance (Fig. 1) (Tserkovnyak *et al.*, 2002). Spin-mixing conductance enables the generation of magnon spin currents by injecting conduction electron spin currents into magnetic materials. It also enables the detection of magnon spin currents by converting them into conduction electron spin currents. This interconversion is essential in SSE and its reciprocal phenomenon, i.e., the spin Peltier effect (SPE) (Flipse *et al.*, 2014; Daimon *et al.*, 2016).

Transport Phenomena in Spin Caloritronics

Thermo-Spin Effect

The thermo-spin effect refers to the interconversion between spin and heat currents, which is the main areas of discussion in the field of spin caloritronics. As representative examples of thermo-spin effects, we demonstrate the fundamentals of thermo-spin conversion phenomena based on conduction electron transport ("Spin-dependent Seebeck and Peltier Effects") and magnon transport ("Spin Seebeck and Peltier Effects").

Spin-dependent Seebeck and Peltier effects

Let us recall the longitudinal electron transport in a conductor. The charge current density (j_c) and heat current density (j_q) are driven by the electrochemical potential gradient ($\nabla\mu$) and temperature gradient (∇T). The linear-response transport can be expressed as

$$\begin{pmatrix} j_c \\ j_q \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} -\nabla\mu/e \\ -\nabla T \end{pmatrix}, \quad (6)$$

where the magneto-thermoelectric effects are not explicitly described. In general, the Onsager reciprocal relation holds between the

off-diagonal components of the transport coefficient matrix, L_{12} and L_{21} , which correspond to the Seebeck and Peltier effects, respectively.

The conduction electron spin current with density $\mathbf{j}_s$ extends electron transport phenomena. Transport phenomena in ferromagnetic conductors are often represented by up- and down-spin electron flows when the spin quantization axis is fixed. Here, the electrical conductivity, (electronic) thermal conductivity, and Seebeck and Peltier coefficients exhibit spin dependence. For example, the electrical conductivity of up-spin electrons $\sigma_\uparrow$ is different from that of down-spin electrons $\sigma_\downarrow$ in ferromagnetic conductors. Driving forces in the spin-dependent electron transport are spin-dependent electrochemical potential gradients, $\nabla\mu_{\uparrow,\downarrow}$, and ∇T , and the transport equation is expressed as

$$\begin{pmatrix} \mathbf{j}_c \\ \mathbf{j}_s \\ \mathbf{j}_q \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{pmatrix} \begin{pmatrix} -\nabla(\mu_\uparrow + \mu_\downarrow)/e \\ -\nabla(\mu_\uparrow - \mu_\downarrow)/e \\ -\nabla T \end{pmatrix}, \quad (7)$$

where $-\nabla(\mu_\uparrow + \mu_\downarrow)/e$ corresponds to $-\nabla\mu/e$ in Eq. (6) and $-\nabla(\mu_\uparrow - \mu_\downarrow)/e$ is the driving force caused by the gradient of spin accumulation ($\mu_\uparrow - \mu_\downarrow$). The heat current and conduction electron spin current are directly coupled if the off-diagonal components of Eq. (7) are finite. For example, if the M_{23} component is finite, a conduction electron spin current is generated by a temperature gradient. This phenomenon is known as the spin-dependent Seebeck effect because it is driven by the spin dependence of the Seebeck coefficient. Eq. (7) holds the Onsager reciprocal relations, and thermo-spin effects that correspond to each off-diagonal component exist. Most of these phenomena have been experimentally observed. In 2010, Slachter *et al.* used nonlocal spin-injection/detection methods in a lateral spin-valve structure and successfully observed the spin accumulation induced by the temperature difference between the ferromagnetic/paramagnetic metal interfaces (Slachter *et al.*, 2010). This is the first study to report the direct detection of the spin-dependent Seebeck effect. Le Breton *et al.* (2011) demonstrated temperature-gradient-induced spin injection into Si via a tunnel junction, which is known as the Seebeck spin tunneling, in a ferromagnetic metal/oxide/Si junction system. Flipse *et al.* (2012) observed the spin-dependent Peltier effect, the reciprocal of the spin-dependent Seebeck effect, in a nanopillar spin-valve device that includes two ferromagnetic metal layers separated by a non-magnetic metal. Subsequently, Dejene *et al.* (2013) reported a nonequilibrium temperature difference between up- and down-spin electrons, known as spin heat accumulation, in a similar nanopillar device (note that Eq. (7) does not contain the spin heat accumulation, which can be phenomenologically discussed by adding the spin index to temperature). The spin-heat current conversion phenomena described in Eq. (7) appear only in itinerant electron systems. Their mechanisms are different from those of SSE and SPE, as described in the next subsection.

Spin Seebeck and Peltier effects

The development of spin caloritronics was accelerated by the discovery of SSE, in which a spin current is generated owing to the application of a temperature gradient to a junction system comprising a magnetic material and conductor. As the first experiment on SSE (Uchida *et al.*, 2008) was performed using a junction of a ferromagnetic metal ($\text{Ni}_{81}\text{Fe}_{19}$) and paramagnetic metal (Pt), SSE was initially discussed in terms of spin transport by conduction electrons, i.e., the spin-dependent Seebeck effect, which occurs only in metals and semiconductors. However, in 2010, it was experimentally demonstrated that SSE occurs in a magnetic insulator, in which transport by conduction electrons is completely frozen (Uchida *et al.*, 2010a,b). These experiments upset the conventional interpretation and revealed that SSE originates from thermally excited magnon transport because magnons can carry spin currents even in insulators (Xiao *et al.*, 2010; Adachi *et al.*, 2011; Hoffman *et al.*, 2013; Rezende *et al.*, 2014; Cornelissen *et al.*, 2016). Since the discovery of SSE in magnetic insulators, experimental techniques and theoretical understanding of this phenomenon have drastically developed. In recent times, most SSE experiments were performed using magnetic insulators because insulator-based systems help achieve a relatively large heat-spin current conversion capability and separate the contribution of conduction-electron-driven magneto-thermoelectric effects from the magnon-spin-current contribution, enabling systematic and reliable investigations of SSE (Uchida *et al.*, 2016). Although the terminologies of thermo-spin effects may be confusing because of historical reasons, SSE and the spin-dependent Seebeck effect are different phenomena. Moreover, the same situation applies to magnon-driven SPE and the conduction-electron-driven spin-dependent Peltier effect (Fig. 1).

The basic mechanism and behavior of SSE are summarized as follows: A typical system used to measure SSE is a junction structure consisting of a ferrimagnetic insulator YIG and paramagnetic metal Pt. When ∇T is applied to YIG, a magnon spin current is generated along the gradient due to the thermally excited dynamics of the localized magnetic moments (Fig. 3(a)). The magnon spin current in YIG is converted into a conduction electron spin current with spatial direction $\mathbf{J}_s$ and spin polarization vector $\mathbf{s}$ in the Pt layer via the spin-mixing conductance at the Pt/YIG interface, where $\mathbf{J}_s$ is normal to the Pt/YIG interface plane and $\mathbf{s}$ is parallel to $\mathbf{M}$ of YIG. Then, the conduction electron spin current in the Pt layer is converted into the charge current $\mathbf{J}_c$ by the strong spin-orbit interaction, satisfying the following symmetry:

$$\mathbf{J}_c \propto \mathbf{s} \times \mathbf{J}_s. \quad (8)$$

This spin-to-charge current conversion is known as the inverse spin Hall effect (ISHE) because the conversion of a charge current into a conduction electron spin current via the spin-orbit interaction is SHE (Fig. 1) (Sinova *et al.*, 2015). As ISHE enables the detection of spin currents as voltage signals, it is extensively used to measure spin-current-induced phenomena. The symmetry of ISHE causes the SSE thermopower to be generated in the direction perpendicular to ∇T and $\mathbf{M}$; hence, SSE can function as a transverse thermoelectric generator (Kirihaara *et al.*, 2012; Uchida *et al.*, 2016). In SSE experiments, the metallic layer must be a thin

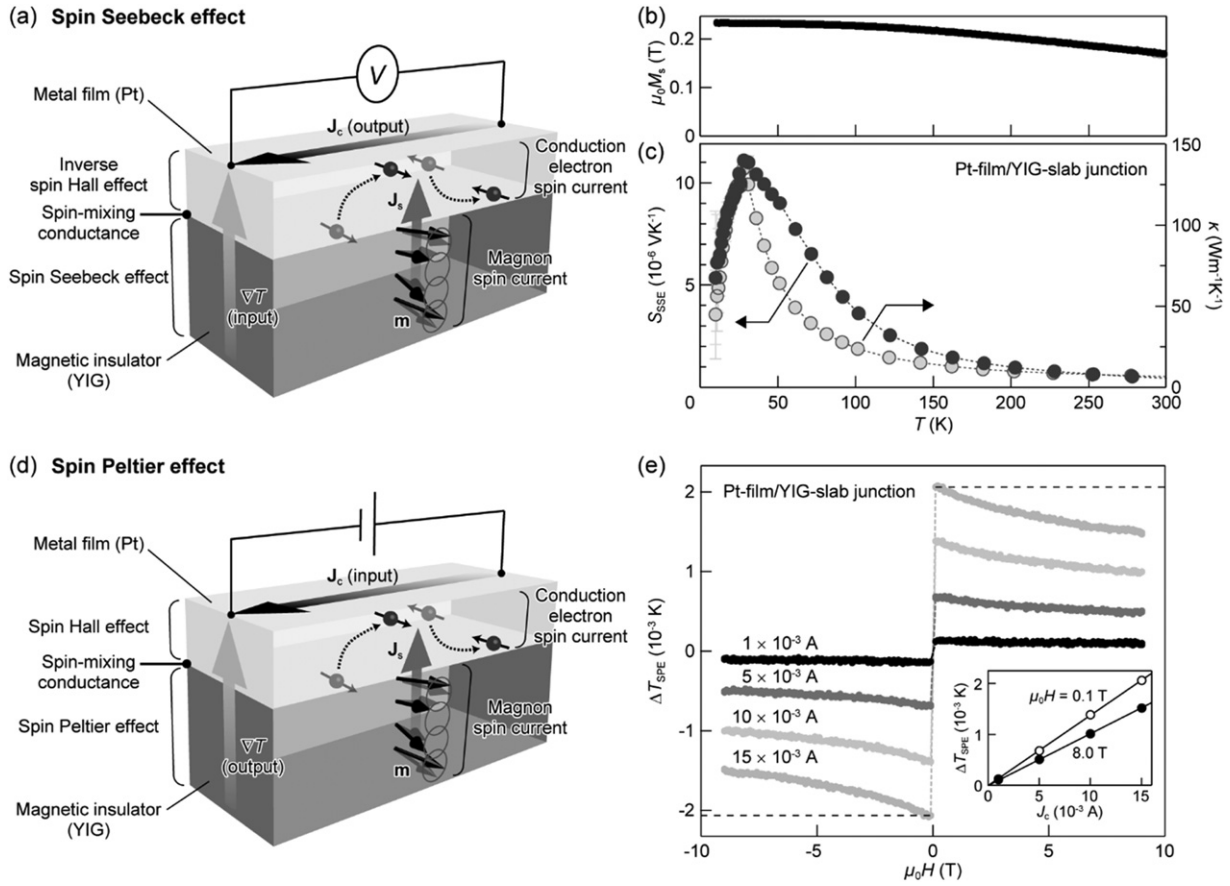


Fig. 3 (a) Schematic of SSE in a junction system that comprises a magnetic insulator (e.g., YIG) and a metal film (e.g., Pt). J_c , J_s , and ∇T denote the charge current, spatial direction of the spin current, and temperature gradient, respectively. (b) Temperature (T) dependence of the saturation magnetization M_s of YIG. (c) T dependence of the transverse thermopower induced by SSE S_{SSE} in the Pt-film/YIG-slab junction system and the thermal conductivity κ of YIG. (d) Schematic of SPE in a junction system that comprises a magnetic insulator and a metal film. (e) Magnetic field (H) dependence of the temperature change induced by SPE ΔT_{SPE} in the Pt-film/YIG-slab system for various values of the input charge current J_c . μ_0 is the vacuum permeability. The inset to (e) shows the J_c dependence of ΔT_{SPE} at $\mu_0 H = 0.1$ and 8.0 T. Experimental details are given in Iguchi *et al.* and Itoh *et al.* Reproduced from Iguchi, R., Uchida, K., Daimon, S., Saitoh, E., 2017. Concomitant enhancement of the longitudinal spin Seebeck effect and the thermal conductivity in a Pt/YIG/Pt system at low temperatures. *Phys. Rev. B* 95, 174401. Itoh, R., Iguchi, R., Daimon, S., *et al.*, 2017. Magnetic-field-induced decrease of the spin Peltier effect in Pt/Y₃Fe₅O₁₂ system at room temperature. *Phys. Rev. B* 96, 184422.

film with a thickness comparable with the spin diffusion length for the efficient conversion of spin currents into voltage signals. In contrast, both bulk and thin-film materials can be used as the magnetic insulator. As the magnitude of the SSE-induced spin current depends on the propagation length of subthermal magnons, the ISHE voltage caused by SSE increases with an increase in the thickness of the magnetic insulator and saturates at a thickness of several micrometers in single-crystalline YIG (Kikkawa *et al.*, 2015; Kehlberger *et al.*, 2015). Thus, the combination of SSE with ISHE enables transverse thermoelectric generation using insulators, which cannot be realized with conventional thermoelectric effects.

The typical temperature-dependent behavior of the SSE-induced transverse thermopower, i.e., the ISHE voltage induced by SSE, is demonstrated in Fig. 3(c) (Iguchi *et al.*, 2017). The sample system used in the experiment is a junction comprising a single-crystalline YIG slab and Pt thin film. The SSE thermopower has been observed at temperatures lower than the Curie temperature of YIG and has disappeared at absolute zero temperature. The temperature dependence of the SSE thermopower is completely different from the magnetization curve of YIG (compare Fig. 3(b) and (c)). When single-crystalline YIG is used, the SSE thermopower increases with a decrease in the temperature and exhibits a peak at ~ 30 K. The temperature at which the thermopower reaches its maximum level is comparable to that at which the thermal conductivity of single-crystalline YIG reaches its maximum level, where the thermal conductivity of YIG is determined mainly by phonon transport. Therefore, the steep peak signal may be related to the phonon drag effect on SSE (Adachi *et al.*, 2010; Jaworski *et al.*, 2011). There is also another argument that the low-temperature enhancement of the SSE thermopower is determined not only by the phonon drag effect but also by the enhancement of the magnon propagation length because the temperature dependences of the SSE thermopower and thermal conductivity differ at temperatures higher than the peak temperature. Although YIG is mainly used in spin caloritronics, SSE has been observed in

various materials, e.g., ferro(ferri)magnetic, paramagnetic (Wu *et al.*, 2015), antiferromagnetic (Seki *et al.*, 2015; Wu *et al.*, 2016), multiferroic (Takagi *et al.*, 2016), and quantum spin materials (Hirobe *et al.*, 2017), indicating that SSE is a universal transport phenomenon that occurs in various materials.

The Onsager reciprocal of SSE is SPE, in which a heat current is generated as a result of a spin current (Fig. 1). This phenomenon was first experimentally observed in (Flipse *et al.*, 2014), where Pt/YIG junction systems were used. As illustrated in Fig. 3(d), SPE occurs through the inverse process of SSE. When J_c is applied to the Pt film, a conduction electron spin current is generated by SHE along the direction of the film thickness, and spin accumulation occurs near the Pt/YIG interface. The spin accumulation is polarized in a direction that satisfies

$$\mathbf{J}_s \propto \mathbf{s} \times \mathbf{J}_c. \quad (9)$$

This spin accumulation is converted into a magnon spin current in YIG via the spin-mixing conductance. The heat current generation due to the magnon spin current is SPE. When $\mathbf{s}$ in the Pt layer is parallel or antiparallel to $\mathbf{M}$ of YIG, the amplitude of the magnetic moment precession in YIG changes owing to the transfer of the spin angular momentum, which modulates the number of magnons. An increase (decrease) in the number of magnons corresponds to the high (low) effective temperature of the magnon system. Therefore, the temperature near the Pt/YIG interface changes owing to the non-equilibrium state induced by the spin current injection. However, when $\mathbf{s}$ and $\mathbf{M}$ are orthogonal, no temperature change occurs. Thus, the heat current (J_q) generated by SPE follows

$$J_q \propto (\mathbf{s} \cdot \mathbf{M})\mathbf{n}, \quad (10)$$

where $\mathbf{n}$ is the normal vector of the junction interface. In addition to this phenomenological discussion, theoretical studies on SPE can be found, for example, in (Basso *et al.*, 2016; Ohnuma *et al.*, 2017; Costa and Sampaio, 2020).

As the observation of SPE requires highly sensitive and accurate temperature measurements for thin-film devices, it becomes more challenging compared to that of SSE experiments. Few experimental studies on SPE were reported for several years after its discovery until the establishment of versatile measurement methods for the spin-current-induced temperature change. In Daimon *et al.* (2016), the SPE-induced temperature change and its unique spatial distribution were visualized using an active infrared emission microscopy technique known as lock-in thermography (LIT). The LIT method helps measure SPE with high temperature and spatial resolutions in a simple sample structure, which does not require micro/nanofabrication techniques. Based on the knowledge obtained from the LIT measurements, SPE was subsequently observed using a thermocouple sensor (Itoh *et al.*, 2017) and lock-in thermoreflectance method (Yamazaki *et al.*, 2020). Fig. 3(e) shows the direct measurement of the SPE-induced temperature change by attaching a thin thermocouple to the surface of a Pt/YIG junction system (Itoh *et al.*, 2017). This result indicates that the temperature change increases in proportion to the charge current applied to the Pt layer and the sign of the temperature change is reversed in response to the $\mathbf{M}$ reversal of YIG. The temperature change signal is suppressed when a strong magnetic field is applied. This behavior results from the suppression of the thermal excitation of magnon spin currents due to the Zeeman gap under a strong magnetic field (Kikkawa *et al.*, 2015). Systematic studies on SPE using various measurement techniques have led to the elucidation of its behavior.

Magneto-Thermoelectric Effect

In addition to the conventional Seebeck and Peltier effects, various thermoelectric conversion phenomena occur in conductors in the presence of magnetic field $\mathbf{H}$ or in a magnetic material with spontaneous $\mathbf{M}$. This phenomenon includes the magneto-Seebeck/Peltier effect, in which the Seebeck/Peltier coefficient depends on the magnitude of $\mathbf{H}$ or the direction of $\mathbf{M}$, and the Nernst (Ettingshausen) effect, in which the heat (charge) current induces a transverse charge (heat) current perpendicular to $\mathbf{H}$ or $\mathbf{M}$ (Fig. 2). In magnetic conductors, magneto-thermoelectric effects appear, even in the absence of an external magnetic field, owing to the effect of the spin-orbit interaction on spin-polarized conduction electrons. Although these magneto-thermoelectric effects are known for a long time, some of these phenomena have not been thoroughly investigated. Magneto-thermoelectric effects are yet to be fully explored from the viewpoints of fundamental physics and applications. Hereafter, we omit the detailed explanations of magnetic-field-dependent effects and focus on magnetization-dependent effects.

As shown in Fig. 2, the conversion between charge and heat currents in magnetic materials is classified into two categories: longitudinal and transverse effects, in which the output current is generated along directions parallel and perpendicular to the input current, respectively. The most well-known longitudinal electric transport phenomenon is anisotropic magnetoresistance, where the electrical resistivity changes depending on the angle θ_M between the $\mathbf{M}$ direction and the input current (McGuire and Potter, 1975). Due to the anisotropic magnetoresistance, in isotropic magnetic materials, the θ_M dependence of the electrical resistivity (ρ) follows

$$\rho(\theta_M) = \rho_{\perp} + (\rho_{\parallel} - \rho_{\perp}) \cos^2 \theta_M, \quad (11)$$

where $\rho_{\parallel}$ ($\rho_{\perp}$) is the electrical resistivity when $\mathbf{M}$ is parallel to (perpendicular to) the input charge current. Moreover, the most well-known transverse electric transport phenomenon is the anomalous Hall effect, where the charge current is bent in the direction perpendicular to $\mathbf{M}$ (Nagaosa *et al.*, 2010). Similar to these phenomena, the thermoelectric conversion properties of magnetic materials depend on the $\mathbf{M}$ direction.

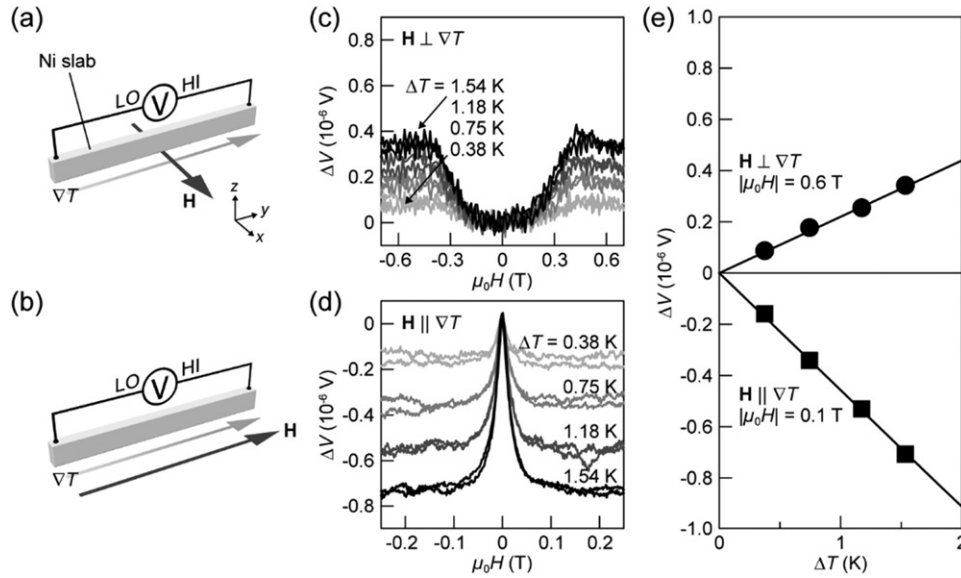


Fig. 4 (a),(b) Setups to measure AMSE. The electric voltage between the ends of the Ni slab along the temperature gradient was measured with applying magnetic field $\mathbf{H}$ along the direction perpendicular or parallel to ∇T . (c),(d) H dependence of the voltage ΔV in the Ni slab for various values of the temperature difference ΔT , measured for the $\mathbf{H} \perp \nabla T$ and $\mathbf{H} \parallel \nabla T$ configurations. The voltage offset caused by the H -independent thermopower was subtracted. The magnitude of the AMSE signal in the $\mathbf{H} \parallel \nabla T$ configuration is twice as large as that in the $\mathbf{H} \perp \nabla T$ configuration. (e) ΔT dependence of ΔV in the Ni slab at $\mu_0 H = 0.6$ T (0.1 T) in the $\mathbf{H} \perp \nabla T$ ($\mathbf{H} \parallel \nabla T$) configuration. Experimental details are given in Uchida *et al.* Reproduced from Uchida, K., Daimon, S., Iguchi, R., Saitoh, E., 2018. Observation of anisotropic magneto-Peltier effect in nickel. *Nature* 558, 95–99.

Longitudinal magneto-thermoelectric effect

Longitudinal magneto-thermoelectric effects in magnetic materials are known as the anisotropic magneto-Seebeck effect (AMSE) and anisotropic magneto-Peltier effect (AMPE), where the Seebeck and Peltier coefficients depend on θ_M , respectively (Jan, 1957; Das *et al.*, 2016). The θ_M dependence of the Seebeck coefficient S is similar to that of the anisotropic magnetoresistance. If the magnetic material is isotropic, the symmetry of S is expressed as

$$S(\theta_M) = S_{\perp} + (S_{\parallel} - S_{\perp}) \cos^2 \theta_M, \quad (12)$$

where $S_{\parallel}$ ($S_{\perp}$) is the Seebeck coefficient when $\mathbf{M}$ is parallel to (perpendicular to) the input heat current. AMSE has been observed in various magnetic materials and nanostructures. Such observations and the Onsager reciprocal relation ($\Pi = ST$, with Π being the Peltier coefficient) indicate the existence of AMPE. The direct observation of the temperature modulation induced by AMPE revealed unconventional thermoelectric conversion functionalities of this phenomenon. For instance, AMPE enables reconfigurable electronic cooling/heating in a single material without junction structures, which cannot be realized if the conventional Peltier effect is used.

Fig. 4 shows the experimental results of AMSE in a polycrystalline Ni slab with a rectangular shape (Uchida *et al.*, 2018). The electrical voltage between the ends of the Ni slab was measured at room temperature by applying temperature gradient ∇T along the y direction and $\mathbf{H}$ (with magnitude H) along the direction perpendicular or parallel to the ∇T direction (Fig. 4(a) and (b)). Fig. 4(c) and (d) show the voltage difference (ΔV) in the Ni slab as a function of H for various values of the temperature difference (ΔT), where ΔV was obtained by removing the voltage offset caused by the H -independent thermopower. The ΔV signals exhibit H -even dependence; the magnitude of ΔV in Ni increases (decreases) with an increase in $|H|$ when $\mathbf{H} \perp \nabla T$ ($\mathbf{H} \parallel \nabla T$) (Fig. 4(c) and (d)) and the field-induced change of ΔV is proportional to ΔT (Fig. 4(e)). Importantly, the ΔV signals in the $\mathbf{H} \perp \nabla T$ ($\mathbf{H} \parallel \nabla T$) configuration saturate at $\mu_0 H = 0.4$ T (0.1 T), which corresponds to the saturation field of the Ni slab (note that the difference in the saturation field is caused by the shape magnetic anisotropy). This result indicates that the behavior of ΔV is determined by $\mathbf{M}$ instead of $\mathbf{H}$. The H -even dependence of thermopower is a feature of AMSE (see Eq. (12)). The anisotropy of the Seebeck coefficient in the Ni slab is estimated to be $\sim 3\%$ at room temperature. As explained above, AMSE can be investigated by measuring the magnetic field dependence of longitudinal thermopower. There are many experimental reports on the observation of AMSE, and such measurements are well established.

Meanwhile, the direct observation of AMPE requires unconventional thermal measurement techniques. In Uchida *et al.* (2018), temperature modulation induced by AMPE was observed using the LIT method. In thermoelectric measurements based on LIT, the spatial distribution of infrared radiation thermally emitted from the surface of a sample is detected using an infrared camera while applying square-wave-modulated AC charge current J_c with amplitude J_c , frequency f , and zero DC offset to the sample. Thermal images oscillating at the same frequency as the input charge current are obtained using the Fourier analysis. The contribution of

thermoelectric effects ($\propto J_c$) can be separated from the Joule-heating background ($\propto J_c^2$) by extracting the first harmonic response of the thermal images because the Joule heating generated under this condition is constant with time. As a result of the Fourier analysis, the obtained thermal images are transformed into lock-in amplitude and phase images, which exhibit the distributions of the magnitude and sign of the current-induced temperature modulation, respectively. The lock-in phase image also includes information on the time delay of the temperature modulation caused by thermal diffusion.

The heat release and absorption induced by AMPE appear on the boundaries between the areas with different θ_M values, even in the absence of material junction structures. A simple way to create such boundaries is to form a non-uniform magnetization configuration (Fig. 5(a)). However, non-uniform magnetization configurations are not suitable for systematic measurements because it becomes difficult to change the magnetization distribution with high controllability. Therefore, the temperature modulation induced by AMPE was observed in uniformly magnetized U-shaped materials, where a charge current was applied along the U-shaped structure (Fig. 5(b)). This configuration leads to a non-uniform θ_M distribution; the AMPE-induced temperature modulation appears around the corners of the U-shaped structure, i.e., the regions between the areas satisfying $\mathbf{M} \perp \mathbf{J}_c$ and $\mathbf{M} \parallel \mathbf{J}_c$. Fig. 5(d) shows the experimental results of AMPE in a polycrystalline Ni film with a U-shaped structure; the results were obtained using the LIT technique (Das *et al.*, 2019). The LIT images were measured while applying $\mathbf{H}$ to the x - y plane at the azimuthal angle θ_H from the $+x$ direction (Fig. 5(f)). The pure AMPE contribution was separated from other thermoelectric contributions by measuring the dependence of the LIT images on the sign and/or angle of the magnetic field. When $\theta_H = 0^\circ$, clear temperature-modulation signals appeared predominantly around the corners (areas 2 and 4 in Fig. 5(f)) of the U-shaped structure. The sign of the temperature modulation in area 2 is opposite to that in area 4 because of the lock-in phase difference of $\sim 180^\circ$. The sign of the AMPE signal is reversed at $\theta_H = 90^\circ$, the signal disappears at $\theta_H = 45^\circ$, and the θ_H dependence of the AMPE signals follows the $\cos 2\theta_H$ symmetry (Fig. 5(e)). This behavior is consistent with Eq. (12) based on the trigonometric relations between θ_M and θ_H . As demonstrated here, AMPE enables thermoelectric cooling and heating in a single material without junction structures. Owing to the absence of junctions, the thermoelectric output of AMPE can be enhanced by constructing simple thermopile structures (Das and Uchida, 2019) and reconfigured by changing the shape of magnetic materials or the magnetization configuration. These characteristics help derive new concepts of thermal management technologies for electronic and spintronic devices.

As the thermoelectric performance of AMSE/AMPE is very low compared with that of conventional thermoelectric devices, it is necessary to find or develop magnetic materials with large anisotropy in the Seebeck and Peltier coefficients. To improve the thermoelectric performance, AMSE/AMPE was measured for various ferromagnetic metals (Miura *et al.*, 2020). Although Ni exhibits clear anisotropy in the Seebeck/Peltier coefficient, AMSE/AMPE in polycrystalline Fe is negligibly small. This behavior was quantitatively reproduced by first-principles-based Boltzmann transport calculations, which clarified that spin-flip electron transitions caused by the spin-orbit interaction are the key mechanisms in AMSE/AMPE (Masuda *et al.*, 2019). The magnitude of the AMSE/AMPE signals in $\text{Ni}_{95}\text{Pt}_5$ and $\text{Ni}_{95}\text{Pd}_5$ was larger than that in pure Ni; the anisotropy of the Seebeck/Peltier coefficient of $\text{Ni}_{95}\text{Pt}_5$ reached $\sim 12\%$. However, the experiments showed that excess Pt and Pd decreased the anisotropy of the coefficient. These results indicate that the doping of heavy elements with strong spin-orbit interactions to ferromagnetic materials can improve the thermoelectric conversion efficiency of AMSE/AMPE; however, the material dependence in such alloys is not fully understood. Materials science studies to find magnetic materials that exhibit large AMSE/AMPE are in progress. It was predicted that several ferromagnetic ordered alloys exhibit very large anisotropy in the Seebeck/Peltier coefficient (Masuda *et al.*, 2019). Experimental demonstration of this prediction is desirable.

Transverse magneto-thermoelectric effect

This section summarizes the basic behaviors and research trends of the transverse magneto-thermoelectric effects, known as the anomalous Nernst effect (ANE) and anomalous Ettingshausen effect (AEE), are summarized. In ANE (AEE), an input heat (charge) current induces a transverse charge (heat) current in a magnetic material along the direction perpendicular to $\mathbf{M}$. The symmetries of ANE and AEE are respectively expressed as

$$\mathbf{j}_{c,ANE} = \sigma S_{ANE}(\mathbf{m} \times \nabla T), \quad (13)$$

$$\mathbf{j}_{q,AEE} = \sigma \Pi_{AEE}(\mathbf{m} \times \nabla V), \quad (14)$$

where $\mathbf{j}_{c,ANE}$ ($\mathbf{j}_{q,AEE}$) is the charge (heat) current density driven by ANE (AEE), $\mathbf{m}$ is the unit vector of $\mathbf{M}$, S_{ANE} (Π_{AEE}) is the anomalous Nernst (Ettingshausen) coefficient, σ is the electrical conductivity, and ∇T (∇V) is the temperature gradient (electric field) applied to the magnetic material. The relation between the anomalous Nernst and Ettingshausen coefficients are

$$\Pi_{AEE} = S_{ANE}T, \quad (15)$$

which is the Onsager reciprocal relation for the transverse thermoelectric conversion in magnetic materials. Based on this symmetry, ANE/AEE exhibits a convenient scaling law that is different from that of longitudinal thermoelectric effects. In the case of ANE, the output voltage (power) can be increased by elongating the device length (enlarging the device area) perpendicular to the temperature gradient without forming a multitude of serial p-n junctions. Furthermore, the thermoelectric output of ANE/AEE can be actively controlled by manipulating $\mathbf{M}$. Thus, ANE (AEE) has the potential to realize simple and versatile thermal energy harvesting or heat-flux sensing (thermal energy management) applications. Although primary studies on ANE/AEE were conducted way back (Bridgman, 1924; Hall, 1925; Butler and Pugh, 1940), the number of studies was quite limited. However, ANE has received renewed attention in spin caloritronics since the discovery of SSE, and experimental methods to separate SSE from ANE have been investigated (Kikkawa *et al.*, 2013a,b). These developments have significantly promoted research on ANE. In particular,

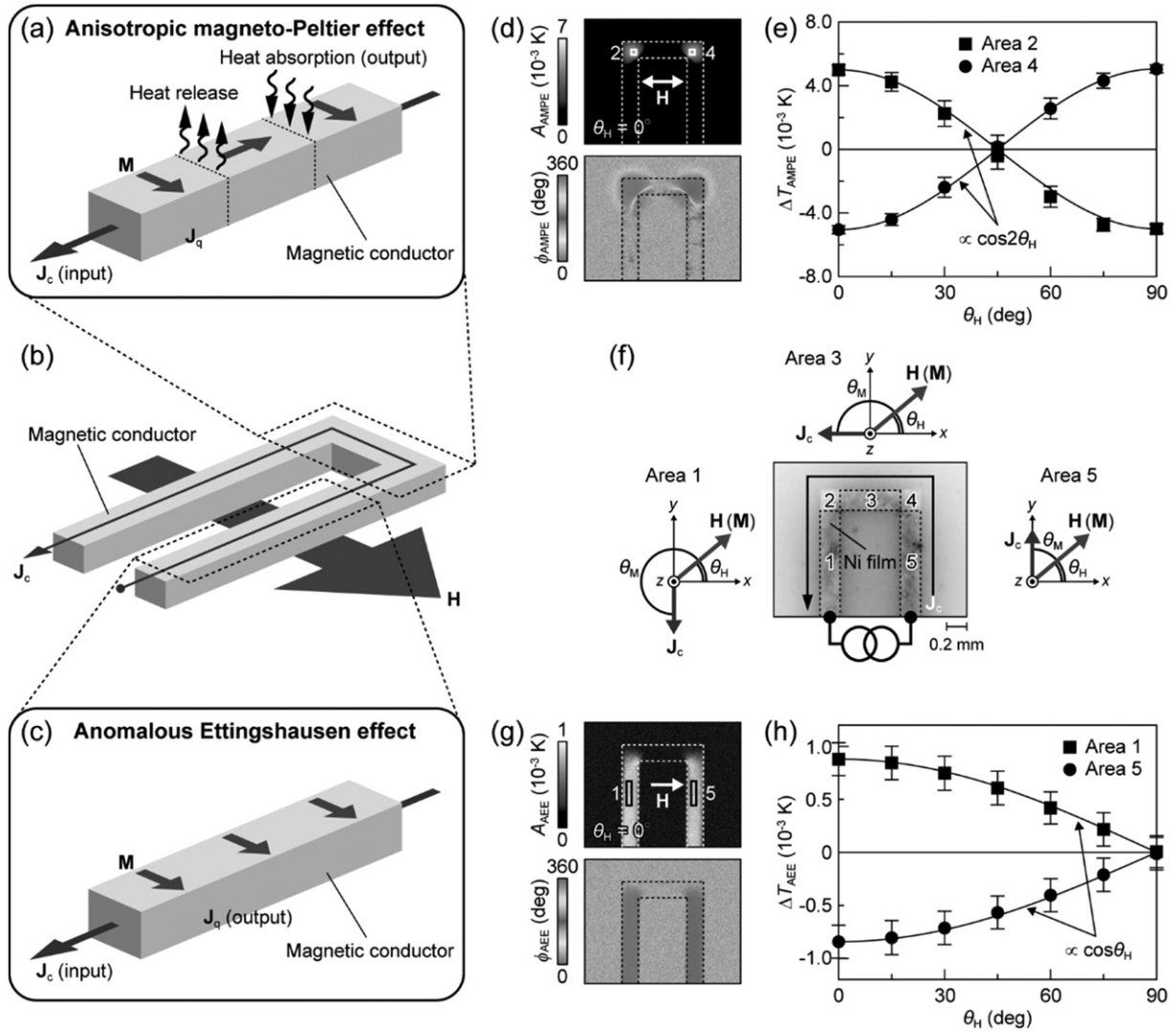


Fig. 5 (a) Schematic of AMPE in a magnetic conductor with non-uniform $\mathbf{M}$ distribution. (b) Schematic of a U-shaped magnetic conductor typically used to measure AMPE and AEE. (c) Schematic of AEE in a uniformly magnetized magnetic conductor. $\mathbf{J}_q$ denotes the heat current induced by the Peltier effect or AEE. (d) Lock-in amplitude A_{AMPE} and phase ϕ_{AMPE} images showing the AMPE-induced temperature modulation for the U-shaped 100-nm-thick Ni film on a glass substrate, measured at a field angle of $\theta_H = 0^\circ$, charge current amplitude of 40 mA, and lock-in frequency of 25 Hz. (e) θ_H dependence of ΔT_{AMPE} ($= A_{\text{AMPE}} \cos \phi_{\text{AMPE}}$) on the areas 2 and 4 of the U-shaped Ni film. The solid curves show the $\cos 2\theta_H$ functions. (f) Steady-state infrared image of the U-shaped Ni film and definitions of θ_H and θ_M . θ_H (θ_M) represents the angle between $\mathbf{H}$ and the $+x$ direction (between $\mathbf{M}$ and $\mathbf{J}_c$), where $\mathbf{M}$ is aligned along $\mathbf{H}$. Areas 1, 3, and 5 are on the regions surrounded by white dotted lines and areas 2 and 4 are on the corner of the U-shaped structure. (g) Lock-in amplitude A_{AEE} and phase ϕ_{AEE} images showing the AEE-induced temperature modulation for the U-shaped 100-nm-thick Ni film on a sapphire substrate, measured at $\theta_H = 0^\circ$, charge current amplitude of 75 mA, and lock-in frequency of 25 Hz. (h) θ_H dependence of ΔT_{AEE} ($= A_{\text{AEE}} \cos \phi_{\text{AEE}}$) on areas 1 and 5 of the U-shaped Ni film. The solid curves show the $\cos \theta_H$ function. Experimental details are given in Das *et al.* Reproduced from Das, R., Iguchi, R., Uchida, K., 2019. Systematic investigation of anisotropic magneto-Peltier effect and anomalous Ettingshausen effect in Ni thin films. Phys. Rev. Appl. 11, 034022.

since the observation of large ANE in magnetic topological materials (Sakai *et al.*, 2018), studies on physics and materials science have further expedited and become a trend in condensed matter physics. In contrast to ANE, AEE has been investigated only in several ferromagnetic metal slabs since the 1920s. This situation was changed by the LIT technique; in Seki *et al.* (2018), the visualization of the AEE-induced temperature modulation in ferromagnetic FePt thin films was reported. Subsequently, AEE has been observed in various materials in both bulk and film forms, where the U-shaped structure is often used to demonstrate the symmetry of AEE (Fig. 5(b) and (c)). AEE measurements using a Ni film are shown in Fig. 5(g) and (h). Using the LIT method, AMPE and AEE can be simultaneously measured and can be separated from each other owing to their different symmetries. In 2019, it was demonstrated that SmCo₅-type permanent magnets exhibit large AEE (Miura *et al.*, 2019).

ANE can be characterized by measuring the H dependence of the transverse thermopower in magnetic materials. Following Eq. (13), the ANE thermopower exhibits an odd dependence on the $\mathbf{M}$ direction, i.e., the H -odd dependence. ANE measurements

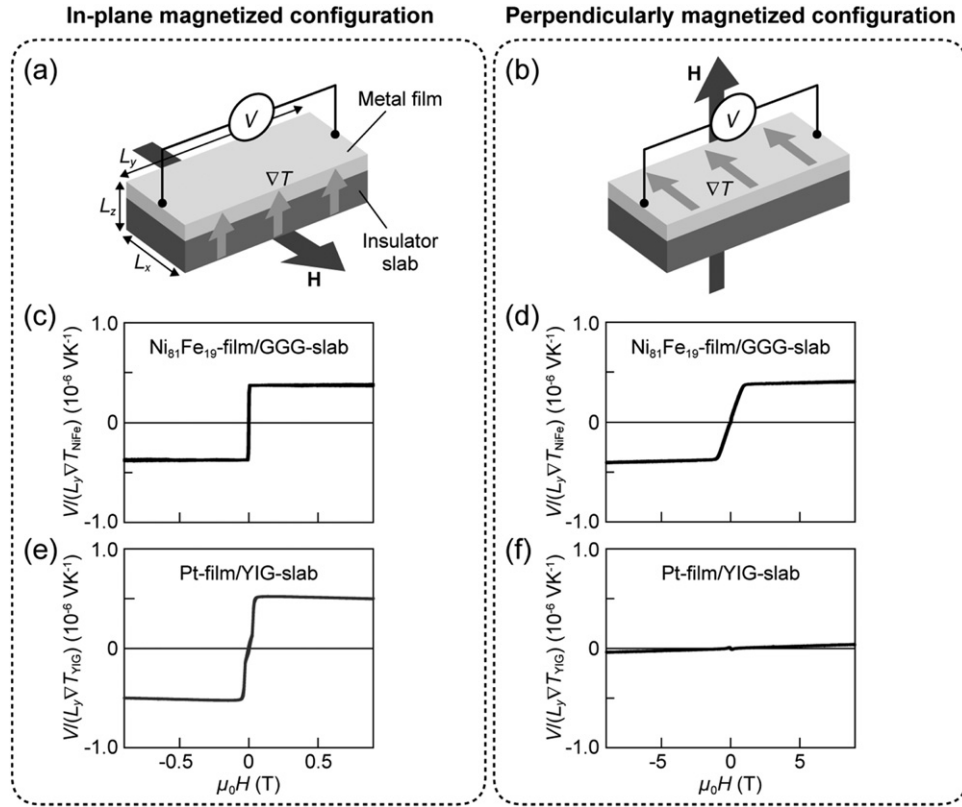


Fig. 6 (a),(b) Schematics of the metal-film/insulator-slab junction system in the in-plane and perpendicularly magnetized configurations. L_x , L_y , and L_z denote the width, length, and thickness of the system, respectively. (c),(d) H dependence of the transverse thermopower $V/(L_y \nabla T_{\text{NiFe}})$ in the $\text{Ni}_{81}\text{Fe}_{19}$ -film/GGG-slab junction system in the in-plane and perpendicularly magnetized configurations. ∇T_{NiFe} denotes the temperature gradient in the $\text{Ni}_{81}\text{Fe}_{19}$ film. (e),(f) H dependence of $V/(L_y \nabla T_{\text{YIG}})$ in the Pt-film/YIG-slab junction system in the in-plane and perpendicularly magnetized configurations. ∇T_{YIG} denotes the temperature gradient in the YIG slab. Experimental details are given in Kikkawa *et al.* Reproduced from Kikkawa, T., Uchida, K., Daimon, S., *et al.*, 2013b. Separation of longitudinal spin Seebeck effect from anomalous Nernst effect: Determination of origin of transverse thermoelectric voltage in metal/insulator junctions. *Phys. Rev. B* 88, 214403.

for thin films were performed in two different configurations due to the significant difference between the in-plane and out-of-plane dimensions. One configuration is the in-plane magnetized configuration, where $\mathbf{H}$ (∇T) is applied along the in-plane (out-of-plane) direction (Fig. 6(a)). The in-plane magnetized configuration is suitable for thermal energy harvesting and heat-flux sensing applications because ANE-based thermoelectric generation can be realized simply by forming films on heat sources. In contrast, it is difficult to quantitatively estimate S_{ANE} in the in-plane magnetized configuration because of the difficulty in estimating the temperature difference between the top and bottom of the thin films (Kikkawa *et al.*, 2013b). The other configuration is the perpendicularly magnetized configuration, where $\mathbf{H}$ (∇T) is applied along the out-of-plane (in-plane) direction (Fig. 6(b)). The perpendicularly magnetized configuration is widely used for the quantitative estimation of S_{ANE} , although it often requires a large magnetic field to align $\mathbf{M}$ of the films along the out-of-plane direction.

Fig. 6(c) and (d) show the H dependence of the transverse thermopower in a ferromagnetic $\text{Ni}_{81}\text{Fe}_{19}$ film formed on a single-crystalline $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ substrate in the in-plane and perpendicularly magnetized configurations, respectively (Kikkawa *et al.*, 2013b). In this experiment, the transverse thermopower is defined as $V/(L_y \nabla T_{\text{NiFe}})$, where V is the voltage between the ends of the $\text{Ni}_{81}\text{Fe}_{19}$ film, ∇T_{NiFe} is the temperature gradient in the film estimated by assuming linear temperature distributions in the film and substrate, and L_y is the length of the sample along the inter-electrode direction. The thermopower exhibits clear H -odd dependence and saturates when $\mathbf{M}$ is aligned along $\mathbf{H}$, indicating that ANE mainly contributes to the transverse thermopower and the field-induced ordinary Nernst effect is negligibly small. The ANE-driven transverse thermopower can be extracted by extrapolating the raw data in the high-field region to zero field.

The comparison of the transverse thermopower between the in-plane and perpendicularly magnetized configurations is often used to separate SSE from ANE (Kikkawa *et al.*, 2013a,b). As shown in Figs. 3(a) and 6(a), in the in-plane magnetized configuration, both SSE and ANE exhibit transverse thermopower, the sign of which is reversed by reversing $\mathbf{M}$. In contrast, in the perpendicularly magnetized configuration, the SSE thermopower disappears because of the symmetry of ISHE (Eq. (8); $\mathbf{J}_s \parallel \mathbf{s}$ in the perpendicularly magnetized configuration), whereas the ANE thermopower can appear because the directions of ∇T , $\mathbf{M}$, and inter-electrode are at right angles to one another. Fig. 6(c-f) show that the $\text{Ni}_{81}\text{Fe}_{19}$ film exhibited comparable ANE thermopower in the

in-plane and perpendicularly magnetized configurations, whereas the Pt/YIG system did not exhibit thermopower in the perpendicularly magnetized configuration, except for the small contribution of the ordinary Nernst effect in the Pt layer. This comparison confirms that SSE in the Pt/YIG system is irrelevant to ANE induced by the magnetic proximity effect in the Pt layer (Huang *et al.*, 2012; Kikkawa *et al.*, 2013a,b) (note that YIG does not exhibit ANE because it is an insulator).

To practically apply ANE, it is important to find and develop magnetic materials with large S_{ANE} . In general, S_{ANE} can be divided into two components as

$$S_{\text{ANE}} = \rho_{xx}\alpha_{xy} + \rho_{xy}\alpha_{xx}, \quad (16)$$

where ρ_{xx} (ρ_{xy}) is the diagonal (off-diagonal) component of the electrical resistivity tensor and α_{xx} (α_{xy}) is the diagonal (off-diagonal) component of the thermoelectric conductivity tensor (Miura *et al.*, 2019; Sakuraba *et al.*, 2020). The second term on the right-hand side of Eq. (16) originates from the anomalous Hall effect due to the longitudinal carrier flow induced by the Seebeck effect. The first term originates from intrinsic ANE because α_{xy} directly converts ∇T into a transverse electric field. A recent trend to improve S_{ANE} is to find materials with large α_{xy} , in which the Berry curvature of the electronic bands near the Fermi level often plays an essential role. Materials with topological band structures, such as Co_2MnGa , demonstrate large values of α_{xy} owing to their large Berry curvature, which, in turn, leads to large S_{ANE} values of 6–8 $\mu\text{V K}^{-1}$ at room temperature (Sakai *et al.*, 2018; Reichlova *et al.*, 2018; Guin *et al.*, 2019; Sumida *et al.*, 2020). Large ANE/AEE in SmCo_5 -type permanent magnets has also been discussed in terms of the intrinsic mechanism (Miura *et al.*, 2019). The current highest S_{ANE} and α_{xy} values are 23 $\mu\text{V K}^{-1}$ and 15 $\text{Am}^{-1}\text{K}^{-1}$ for $\text{UCo}_{0.8}\text{Ru}_{0.2}\text{Al}$, respectively, although this material exhibits ANE only at low temperatures ($< 60\text{K}$) (Asaba *et al.*, 2021). The current record-high figure of merit for ANE is > 0.003 for the noncollinear antiferromagnet YbMnBi_2 at $\sim 170\text{K}$, where anisotropic transport properties play a critical role (Pan *et al.*, 2021). Importantly, in most magnetic materials, the thermoelectric performance of ANE is not correlated with the saturation magnetization; materials science studies to improve ANE performance require strategies and techniques different from conventional magnetics (Uchida *et al.*, 2021). One strategy to enhance ANE/AEE is to optimize magnetic multilayers; ANE in alternately stacked ferromagnetic metal/nonmagnetic metal multilayers was found to be enhanced by increasing the number of interfaces (Uchida *et al.*, 2015; Fang *et al.*, 2016; Ramos *et al.*, 2019; Seki *et al.*, 2021). Although the enhancement of ANE in multilayers seems to be a universal trend, the microscopic mechanism is yet to be clarified. As discussed here, further physics and materials science studies are necessary to realize the thermoelectric applications of ANE/AEE.

Thermomagnetic Effect

Longitudinal and transverse thermomagnetic effects represent magneto-thermal resistance and thermal Hall effects, respectively (Fig. 2). Although these phenomena are still far from being applied, the magneto-thermal resistance and thermal Hall effects have a potential to be applied as thermal switching devices and heat current circulators, respectively (Uchida and Iguchi, 2021).

Magneto-thermal resistance

The magneto-thermal resistance refers to the magnetic field or magnetization dependence of thermal conductivity, which is known as the Maggi–Righi–Leduc effect (Zawadzki, 1962). The magneto-thermal resistance in a magnetic material is the thermal analog of the anisotropic magnetoresistance; the thermal conductivity in the $\mathbf{M} \perp \mathbf{J}_q$ configuration is different from that in the $\mathbf{M} \parallel \mathbf{J}_q$ configuration, where $\mathbf{J}_q$ is the heat current (Kimling *et al.*, 2013). However, the $\mathbf{M}$ -dependent anisotropy of thermal conductivity is small in ferromagnetic metals.

The large magneto-thermal resistance has emerged in magnetic multilayer films that comprise alternately stacked ferromagnetic and nonmagnetic materials. Such multilayer films form the core of spintronic devices because they exhibit giant (tunnel) magnetoresistance when the nonmagnetic layer is a metal (an insulating tunnel barrier). In magnetic multilayer films, the electrical conductivity is larger when the $\mathbf{M}$ directions of the adjacent ferromagnetic layers are aligned parallel than when they are antiparallel owing to the giant/tunnel magnetoresistance, where the $\mathbf{M}$ configuration can be switched by an external magnetic field or spin injection. In magnetic multilayer films, owing to the magneto-thermal resistance, thermal conductivity depends on the $\mathbf{M}$ configuration (Fig. 7) (Jeong *et al.*, 2012; Kimling *et al.*, 2015; Nakayama *et al.*, 2021). Recent experiments have shown that the thermal conductivity switching ratio, $(\kappa_{\text{P}} - \kappa_{\text{AP}})/\kappa_{\text{AP}}$, in magnetic metal multilayers can exceed 100% above room temperature, where κ_{P} (κ_{AP}) is the thermal conductivity for the parallel (antiparallel) magnetization configuration, and the thermal conductivity switching ratio can be larger than the electrical conductivity switching ratio (Nakayama *et al.*, 2021). The magneto-thermal resistance was observed not only in current-perpendicular-to-plane giant magnetoresistance devices, depicted in Fig. 7, but also in current-in-plane devices. As the magneto-thermal resistance in magnetic multilayers is applicable to the thermal management of spintronic devices (Uchida and Iguchi, 2021), further enhancement of the thermal conductivity switching ratio and the elucidation of its microscopic mechanism are required.

Thermal Hall effect

The thermal Hall effect is the thermal analog of the Hall effect, which is known as the Righi–Leduc effect (Zawadzki, 1962). The magnetic-field-dependent and magnetization-dependent thermal Hall effects are often called the ordinary and anomalous thermal Hall effects, respectively, in a similar manner to the Hall effects. When a material exhibits the thermal Hall effect, the heat current is bent along a direction perpendicular to $\mathbf{H}$ or $\mathbf{M}$, where the direction of the transverse heat current is reversed by reversing the $\mathbf{H}$ or $\mathbf{M}$.

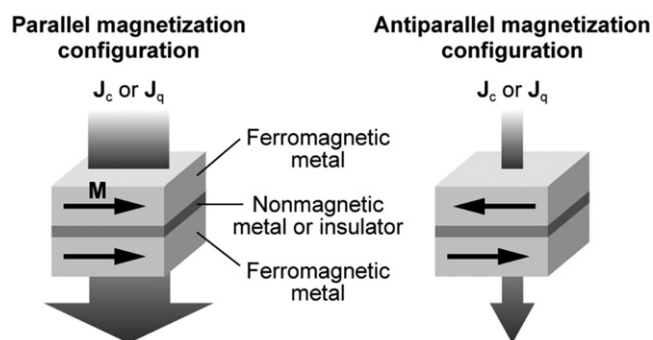


Fig. 7 Schematic of electric and thermal transport phenomena in a giant or tunnel magnetoresistance device. In such multilayer devices, not only the giant/tunnel magnetoresistance and magneto-thermal resistance effects but also the magneto-Seebeck/Peltier effects appear (Shan *et al.*, 2015; Kuschel *et al.*, 2019).

direction. This feature can be regarded as a heat-current circulator. Importantly, the thermal Hall effect occurs not only in conductors but also in insulators, where heat currents are carried by phonons and/or magnons (Strohm *et al.*, 2005; Onose *et al.*, 2010).

Future Directions

As reviewed in the previous sections, novel phenomena, principles, and functionalities based on the interplay between spin, charge, and heat currents have been discovered and investigated in spin caloritronics. This field is still in development, and there are remaining challenges with regard to fundamental physics and materials science. In this section, we discuss the prospect of spin caloritronics based on recent research trends.

Fundamental Physics Viewpoint

One of the developing studies on spin caloritronics is the transverse thermo-spin effect. “Transport Phenomena in Spin Caloritronics” discusses the longitudinal and transverse magneto-thermoelectric/thermomagnetic effects. In contrast, all the aforementioned thermo-spin effects are classified as longitudinal effects because heat and spin currents flow parallel to each other. In recent times, basic studies on transverse thermo-spin effects have been conducted. For example, several groups have reported the observation of the spin Nernst effect, which is the thermal analog of SHE (Meyer *et al.*, 2017; Sheng *et al.*, 2017; Kim *et al.*, 2017). In the spin Nernst effect, a conduction electron spin current is generated in a nonmagnetic conductor via the spin-orbit interaction along the direction perpendicular to the applied temperature gradient. These experiments suggest the existence of the spin Ettingshausen effect, which is the reciprocal of the spin Nernst effect. To understand the microscopic mechanism of the transverse thermo-spin effects and reveal their functionalities, systematic measurements, including temperature and material dependencies, are necessary.

Although conventional spin caloritronics focuses on linear-response transport phenomena, investigations on nonlinear spin caloritronics have been recently initiated. Fundamental thermoelectric effects consist of not only the Seebeck and Peltier effects but also the Thomson effect, which is a representative nonlinear thermoelectric conversion phenomenon proportional to the temperature gradient and charge current applied to a conductor. As the first step in nonlinear spin caloritronics, the direct observation of the magneto-Thomson effect was reported in (Uchida *et al.*, 2020), where a strong magnetic field dependence of the Thomson coefficient appeared in $\text{Bi}_{88}\text{Sb}_{12}$ (Fig. 8). In the nonlinear regime, several spin-caloritronic phenomena, such as electron-driven spin-dependent Thomson and magnon-driven spin Thomson effects, remain to be observed. Exploring these phenomena will further invigorate the fundamental studies on spin caloritronics.

Moreover, the expansion of the physics of spin caloritronics to other fields and materials is important. One of such research directions is polarization caloritronics using ferroelectrics; Bauer *et al.* (2021) theoretically predicted unconventional thermoelectric effects based on the dielectric polarization transport. The experimental verification of such phenomena requires the interdisciplinary fusion of spin caloritronics, ferroelectrics, and nanoscale science. In Phan *et al.* (2021), a new field called opto-spin-caloritronics has been proposed, where 2D van der Waals ferromagnets play an essential role to optically control and enhance thermo-spin conversion properties. Combined with sophisticated interface engineering in magnetic heterostructures, 2D and low-dimensional materials may be key materials in next-generation spin caloritronics.

Materials Science Viewpoint

To realize the application of spin caloritronics, it is necessary to significantly improve the thermo-spin/thermoelectric conversion performance. Thus, it is essential to develop materials with high spin-charge-heat interconversion properties. The recent fusion of spin caloritronics and topological materials science is a part of this effort.

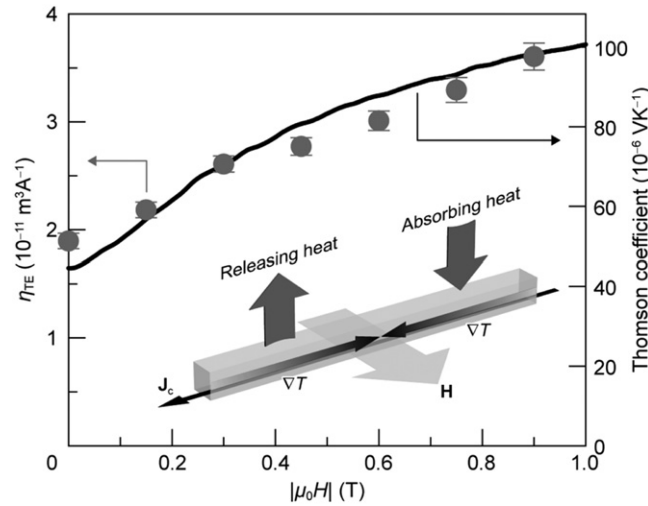


Fig. 8 Magnetic field ($|\mu_0 H|$) dependence of the Thomson-effect-induced temperature modulation normalized by a charge current density and temperature gradient η_{TE} , measured using the LIT method, and the Thomson coefficient for $\text{Bi}_{88}\text{Sb}_{12}$. Experimental details are given in Uchida *et al.* Reproduced from Uchida, K., Murata, M., Miura, A., Iguchi, R., 2020. Observation of the magneto-Thomson effect. *Phys. Rev. Lett.* 125, 106601.

In addition to monolithic materials, hybrid or composite materials can be used to enhance the thermo-spin/thermoelectric conversion performance. For example, the hybrid thermoelectric generation based on SSE and ANE is enabled in ferromagnetic metal/ferrimagnetic insulator junction systems (Kikkawa *et al.*, 2013b; Uchida *et al.*, 2016) and ferromagnetic/nonmagnetic bulk nanocomposites (Boona *et al.*, 2016). Furthermore, Zhou *et al.* proposed and demonstrated the unconventional transverse thermoelectric generation appearing in thermoelectric semiconductor/magnetic metal hybrid materials (Zhou *et al.*, 2021). As this effect originates from the artificial hybridization of the Seebeck effect in the thermoelectric semiconductor and anomalous Hall effect in the magnetic metal, it is called the Seebeck-driven transverse thermoelectric generation. Zhou *et al.* showed that an n-type Si/Co₂MnGa (p-type Si/Co₂MnGa) hybrid material exhibits a transverse thermopower of $82.3 \mu\text{VK}^{-1}$ ($-41.0 \mu\text{VK}^{-1}$) at room temperature, which is much larger than S_{ANE} . These experiments confirmed the usefulness of hybrid or composite materials, which may be a breakthrough approach for the application of spin caloritronics. As hybrid and composite materials are yet to be optimized for spin caloritronics, there are lots of possibilities to improve the spin-charge-heat interconversion efficiency.

Conclusions

We reviewed the interconversion phenomena between spin, charge, and heat currents, i.e., the thermo-spin, magneto-thermoelectric, and thermomagnetic effects. Although only a few examples of such phenomena are introduced in this article, new principles and phenomena have been discovered in spin caloritronics every year. One of the reasons behind this rapid development is that the expression of electron transport phenomena in the 2×2 matrix, which represents the charge and heat currents (Eq. (6)), is extended to the 3×3 matrix by including a conduction electron spin current (Eq. (7)), thereby resulting in a significant increase in the varieties of transport phenomena. Moreover, the introduction of other spin-transport carriers, such as magnons, has resulted in the discovery of various thermo-spin conversion phenomena. The exploration of new principles has motivated numerous experimental and theoretical researchers to study spin-caloritronic phenomena.

What is the significance of spin caloritronics from the viewpoint of its applications? One answer to this question is the use of novel functionalities provided by the spin degree of freedom, which cannot be realized with conventional thermal energy engineering and thermoelectric technologies. By employing the transport phenomena, which have been introduced in this article, various thermoelectric generation and thermal management functionalities can be realized as follows:

- Magnetic-field-induced control of the sign and magnitude of thermopower
- Thermoelectric power generation and cooling using insulators
- Construction of simple thermoelectric conversion modules
- Enhancement of thermoelectric output by enlarging a lateral device area
- Electronic cooling using a single material without junction structures
- Reconfiguration of thermoelectric conversion characteristics by changing the shape of magnetic materials and their magnetization distributions
- Active control of heat current directions and distributions

At present, the thermoelectric conversion efficiency of spin-caloritronic phenomena is much smaller than that of the conventional Seebeck and Peltier effects. However, physics and materials science studies are still in the early stages of development.

Further discovery of new principles and improvements in thermo-spin/thermoelectric conversion efficiencies are expected in the future.

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Advanced Magnetocaloric Materials

Luis M Moreno-Ramírez, Jia Yan Law, Álvaro Díaz-García, and Victorino Franco, Department of Condensed Matter Physics, ICMS-CSIC, University of Sevilla, Sevilla, Spain

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Abstract

Solid-state magnetic refrigeration systems are expected to become commercial in different sectors in the coming years due to their high energy efficiency and lack of toxic/harmful gases. However, at this stage, this new technology needs further developments to commercially compete with the traditional one. Focusing on materials research, this article collects the most promising magnetocaloric materials, either for cryogenic or room temperature applications, paying attention to the underlying thermomagnetic phase transitions, material optimization routes and analysis methods to properly determine the functionality of the materials. To conclude, current trends in the topic are outlined.

Key Points

- Reviews the most promising magnetocaloric materials according to the undergoing thermomagnetic phase transition.
- Displays strategies for materials optimization based on the characteristics of the transition.
- Presents novel analysis methods to determine materials functionality.
- Gives an outlook of current trends in the topic.

Introduction

Solid-state magnetic refrigeration systems offer an energy efficient and green alternative to the current refrigeration devices based on gas compression/expansion (Brück, 2007; Franco *et al.*, 2018; Gutfleisch *et al.*, 2011; Kitanovski *et al.*, 2015). This new technology is based on the significant magnetocaloric effect that some magnetic materials exhibit when subjected to a variable magnetic field (Weiss and Piccard, 1917). In addition to their more environmentally friendly character, magnetocaloric refrigeration systems are found to be around 50 % more energy efficient than conventional ones (Zimm *et al.*, 1998). The first demonstration of the possibilities of this technology for room temperature applications was reported in 1976 by G. Brown with the development of a magnetic heat pump (Brown, 1976). This prototype used Gd as a working magnetocaloric material and magnetic field generators based on superconductors up to 7 T. However, for commercial purposes, there are two main drawbacks: Gd is a critical material and superconductors need cryogenic cooling systems based on liquid He or N₂. Alternatively, permanent magnet arrays can generate useful magnetic fields around 1–2 T (Björk *et al.*, 2010b; Halbach, 1980). There have been some commercial attempts in the last few years, but the lower working temperature and higher price have prevented those prototypes from competing with current refrigerators at the moment. On the other hand, the significance of the magnetocaloric effect at cryogenic temperatures has been clearly demonstrated since 1933, employing Gd₂(SO₄)_{3.8}•H₂O paramagnetic salts and attaining temperatures below 1 K (Giauque and MacDougall, 1933). Nowadays, hydrogen liquefaction for storage and transport is increasing the popularity of magnetocaloric technology in the range of 20–80 K (Kamiya *et al.*, 2006).

The magnetocaloric effect is defined as the reversible temperature/entropy change of a magnetic material produced by the modification of the magnetic field in adiabatic/isothermal conditions, ΔT_{ad} and ΔS_{iso} , respectively (Weiss and Piccard, 1917). These magnitudes vary with temperature and magnetic field change, and are most significant in the temperature range close to a thermomagnetic phase transition. The importance of the characteristics of the phase transition was first established with the discovery of a giant magnetocaloric effect in Gd₅(Si,Ge)₄ associated to a first-order thermomagnetic phase transition, whose response surpassed the second-order response of Gd (Pecharsky and Gschneidner, 1997a). A scheme for illustrating the difference between second- and first-order magnetocaloric materials in a simplified way is depicted in Fig. 1. For second-order materials, the isothermal entropy change coincides with the magnetic one, while this is not true for first-order materials, as these transformations have a remarkable contribution coming from the lattice subsystem (i.e., the latent heat). After the completion of the first-order phase transformation, the magnetocaloric response “saturates” while for second-order transitions, much higher fields are needed (Gottschall *et al.*, 2019a, 2016b). It should be noted that magnetic and lattice contributions can have opposite signs and, therefore, competing effects towards the total response (Gottschall *et al.*, 2016a; Hao *et al.*, 2020b; Law *et al.*, 2019). First-order phase transitions can be further classified into magnetostructural or magnetoelastic phase transitions based on whether they modify the crystal structure of the material. Since the discovery of the giant magnetocaloric effect in Gd₅(Si,Ge)₄, the research efforts for room temperature applications shift to materials exhibiting first-order phase transitions. However, first-order materials have a major drawback: intrinsic hysteresis (Gutfleisch *et al.*, 2016). This hysteresis reduces their applicability in actual refrigerators as the cyclic response can be drastically reduced in comparison to the first shot characterization (Gottschall *et al.*, 2019b). Minimizing

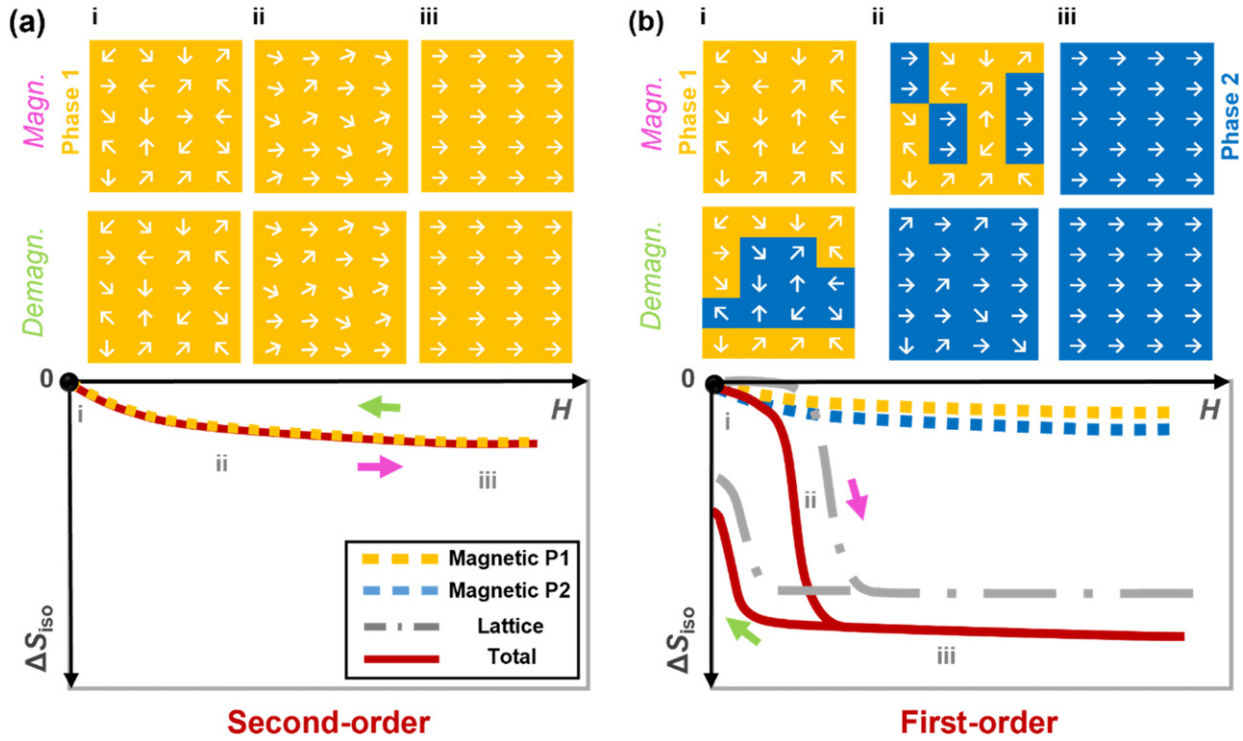


Fig. 1 Illustration of the field dependence of the magnetocaloric effect for materials undergoing either second- (a) or first-order phase transitions (b). Upper panels illustrate magnetization and phase content of the material while magnetizing (abbreviated by magn. and indicated by pink arrows) and demagnetizing (abbreviated by demagn. and indicated by green arrows). Lower panels depict the different contributions to the isothermal entropy change as a function of the magnetic field. (a) For the second-order case, only the magnetic sublattice contributes to the isothermal entropy change leading to higher values as we increase field (from i $\rightarrow$ iii) and the magnetic moments align. The response is fully reversible. (b) For first-order magnetocaloric materials, besides the magnetic contribution, a transformation between two different phases, represented by different colors, with associated latent heat (change in the lattice contribution) takes place. After the transformation is completed, only the magnetic contribution of phase 2 remains up to high fields. This type of transformation is associated with hysteresis, leading to non-reversible magnetocaloric responses, as shown by the difference between stages i and ii while magnetizing and demagnetizing.

hysteresis without deteriorating the magnetocaloric response or exploiting it in multicaloric devices remains a challenge (Gottschall *et al.*, 2018; Gutfleisch *et al.*, 2016). Other critical aspects such as corrosion, mechanical properties, or thermal conductivity also affect material performance and must be properly addressed (Guillou *et al.*, 2014b; Lionte *et al.*, 2021; Navickaitė *et al.*, 2018).

From the Materials Science point of view, the search of new magnetocaloric materials with “improved” performance based on abundant elements remains crucial for the development of the technology. In this article, after an introduction of the magnetocaloric effect and associated magnitudes, a review of the state-of-the-art magnetocaloric materials, categorized according to the undergoing thermomagnetic phase transition, is presented. Possible optimization pathways are discussed as well as methods for characterizing the phase transitions. Presented materials mainly consist of intermetallic bulk materials for large scale applications, although there are interesting results and effects for low dimensional materials (Belo *et al.*, 2019; Evangelisti *et al.*, 2005; Evangelisti and Brechin, 2010; Zhang *et al.*, 2022a). Finally, some novel research lines for overcoming some of the open issues are presented.

Magnetocaloric Magnitudes and Measurements

Both ΔS_{iso} and ΔT_{ad} can be obtained by indirect or direct methods. The most extended methods are the indirect ones as they are based on conventional measurements, such as magnetization, M , and specific heat, c (Neves Bez *et al.*, 2018; Pecharsky and Gschneidner, 1999). On the one hand, ΔS_{iso} can be calculated from magnetization measurements with the following expression derived from Maxwell relations:

$$\Delta S_{iso}(T, \Delta H) = \mu_0 \int_{H_i}^{H_f} \left(\frac{\partial M}{\partial T} \right)_H dH, \quad (1)$$

where T is the temperature, H_i the initial field, H_f the final field, $\Delta H = H_f - H_i$ its increment, and μ_0 the vacuum magnetic

permeability. Magnetization measurements can be either isothermal $M(H)$ or isofield $M(T)$ measurements, being $M(H)$ measurements typically chosen due to its faster speed compared to $M(T)$. However, it is essential to perform a memory erasing protocol prior to each $M(H)$ measurement to avoid spurious data in first-order materials (Caron *et al.*, 2009; Tocado *et al.*, 2009). To obtain ΔT_{ad} by indirect methods, specific heat measurements are typically needed. Combining magnetization and specific heat data, ΔT_{ad} is obtained as follows:

$$\Delta T_{ad}(T, \Delta H) = T \left(\exp \left(-\mu_0 \int_{H_i}^{H_f} \frac{1}{c_H} \left(\frac{\partial M}{\partial T} \right)_H dH \right) - 1 \right), \quad (2)$$

which, if $\Delta T_{ad} \ll T$, can be simplified to:

$$\Delta T_{ad}(T, \Delta H) = -\mu_0 \int_{H_i}^{H_f} \frac{T}{c_H} \left(\frac{\partial M}{\partial T} \right)_H dH. \quad (3)$$

However, this expression is not very useful since $c_H(T)$ should be measured for many fields to have a good numerical approximation. Considering the specific heat as field independent magnitude, it is possible to reach the following expression that combines both magnetocaloric magnitudes:

$$\Delta T_{ad} \approx -\frac{T \Delta s_{iso}}{c_{p,H}}. \quad (4)$$

Despite that this approximation could give reasonable results for second-order phase transitions, it is not appropriate for first-order ones due to the strong temperature and field dependence of c_H in the vicinity of their transformations. It should be highlighted that there are recent methods to obtain ΔT_{ad} from time-dependent magnetometry avoiding heat capacity measurements (Almeida *et al.*, 2022). When the specific heat is measured, it is more rationale to calculate the ΔT_{ad} (and Δs_{iso}) through the obtention of the total entropy as:

$$s_H(T) = \int_{0K}^T \frac{c_{p,H}}{T} dT + s_{0K,H}, \quad (5)$$

where $s_{0K,H}$ refers to the entropy at 0 K. To calculate $s_{0K,H}$, temperatures close to 0 K must be reached. Assuming that $s_{0K,H}$ is small and field independent, its contribution to the magnetocaloric calculations would be negligible. For samples with phase transitions close to room temperature, reaching temperatures close to 0 K during heat capacity measurements can be expensive and time consuming. To avoid this temperature excursion, it is preferable to use optimal initial temperatures that allow accurate measurements to be obtained even when the measurement temperature span is restricted to the environment of the phase transition (Moreno-Ramírez *et al.*, 2018a, 2016). Once the entropy is obtained, both Δs_{iso} and ΔT_{ad} are calculated as:

$$\Delta s_{iso}(T, \Delta H) = [s_{H_f}(T) - s_{H_i}(T)]_T, \quad (6)$$

$$\Delta T_{ad}(T, \Delta H) = [T_{H_f}(s) - T_{H_i}(s)]_{s_{H_i}(T)}, \quad (7)$$

where entropy curves $s(T)$ are inverted to $T(s)$.

As previously mentioned, direct methods are less used than indirect ones because they will require to be performed in dedicated or home-made devices. For quantifying ΔT_{ad} , the most conventional device measures the temperature variations using a thermocouple attached to the sample that is placed in a temperature controlled and isolated environment (Dan'kov *et al.*, 1997; Skokov *et al.*, 2012). It should be emphasized that discontinuous protocols are required when the $\Delta T_{ad}(T, H)$ is directly characterized in first-order materials from isothermal measurements (Moreno-Ramírez *et al.*, 2019a). Other examples of direct setups are based on reciprocating stages (Gopal *et al.*, 1997), optical properties, such as the mirage effect (Cugini *et al.*, 2016) or infrared thermography (Díaz-García *et al.*, 2022; Hirayama *et al.*, 2017). For direct quantification of Δs_{iso} , Peltier cells (Nielsen *et al.*, 2015) or adapted calorimetry setups can be employed (Palacios *et al.*, 2010).

In addition to Δs_{iso} and ΔT_{ad} , there are other magnetocaloric magnitudes that are of interest for performance evaluation. One is the refrigerant capacity, which accounts for the heat that can be exchanged between hot and cold thermal reservoirs. However, as those temperatures are typically unknown, they are substituted by the full width at a half maximum of Δs_{iso} (Wood and Potter, 1985). By doing so, refrigerant capacity values are overestimated for materials with small and broad Δs_{iso} peaks. For solving this, the averaged entropy change, *TEC*, has been proposed (Griffith *et al.*, 2018):

$$TEC(\Delta T_{lift}) = \frac{1}{\Delta T_{lift}} \max_{T_{mid}} \left\{ \int_{T_{mid} - \frac{\Delta T_{lift}}{2}}^{T_{mid} + \frac{\Delta T_{lift}}{2}} \Delta s_{iso} dT \right\}, \quad (8)$$

where ΔT_{lift} is the temperature span of operating temperatures in the intended device (between 3 and 10K) and T_{mid} is the temperature that maximizes the area below the $\Delta s_{iso}(T)$ curve within the selected temperature span. Another interesting magnitude is the exponent of the field dependence of Δs_{iso} (Franco *et al.*, 2006). This exponent, denoted as n , gives important information about the nature of the thermomagnetic phase transitions and is calculated as:

$$n(T, \Delta H) = \frac{d \ln(|\Delta s_{iso}|)}{d \ln(\Delta H)}. \quad (9)$$

For materials undergoing second-order phase transitions, n is related to the critical exponents at the transition (Franco *et al.*, 2008; Franco and Conde, 2010). The use of the exponent n can also be extended to first-order phase transitions, as it offers a quantitative criterion that allows one to distinguish the order of the transformation (Law *et al.*, 2018) and to identify critical compositions (where the materials is transitioning from a first-order to a second-order type) (Franco *et al.*, 2017). The analysis of the exponent n has been proven to be useful in the optimization of magnetocaloric materials and it will be further detailed in this article.

Magnetocaloric Materials

This section lists some of the most promising magnetocaloric materials, being classified according to their thermomagnetic phase transition: (1) second-order, (2) magnetoelastic first-order, and (3) magnetostructural first-order. Maximum values of Δs_{iso} and ΔT_{ad} ($\Delta s_{\text{iso}}^{\text{max}}$ and $\Delta T_{\text{ad}}^{\text{max}}$, respectively) for a moderate magnetic field change of 2 T is employed for comparison when those data are available in the literature.

Second-Order Magnetocaloric Materials

The main advantage of second-order magnetocaloric materials is that they present a fully reversible response, which is highly desired for refrigeration cycles. Due to the nature of the transition, this type of materials fulfils magnetic as well as magnetocaloric scaling relations in the vicinity of the transition (Franco *et al.*, 2006; Franco and Conde, 2010). The magnetocaloric universal curve, mainly applied for Δs_{iso} magnitude, together with the associated critical exponents extracted from it, can give useful information about the materials in a more straightforward way than other methods that require more tedious analyses, such as Kouvel-Fisher (Sánchez-Pérez *et al.*, 2016). Moreover, the good collapse onto a universal curve can be employed as an easy and fast indication of a second-order phase transition (Bonilla *et al.*, 2010).

This category of materials includes Gd, the paradigmatic magnetocaloric material for room temperature magnetic refrigeration. Gd, with a hexagonal close-packed structure, undergoes a ferromagnetic (FM) to paramagnetic (PM) transition. The main quality of Gd is its large magnetic moment, which cannot be easily surpassed. For a magnetic field change of 2 T, it showed a $\Delta s_{\text{iso}}^{\text{max}}$ of $-5.0 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}$ of 5.7 K around 294 K (Pecharsky and Gschneidner, 1997a). However, the criticality of Gd, and rare earth (RE) elements in general, is the factor that prevents an extended use of this material. For identifying critical elements in the listed materials, the supply risk index of the most employed elements is included in Fig. 2 (European Commission, Directorate-General for Internal Market Entrepreneurship and SMEs Industry *et al.*, 2020). One strategy to take advantage of the characteristics of Gd while reducing criticality of the material is to look for Gd-based intermetallic alloys. Some examples of phases with transition temperatures around room temperature are GdZn or Gd₇Pd₃ (Canepa *et al.*, 2002; Gębara *et al.*, 2020). The responses in these Gd-based intermetallics are reduced in comparison to that of Gd, with $\Delta T_{\text{ad}}^{\text{max}}$ of 3.6 and 3.0 K for 2 T obtained for GdZn and Gd₇Pd₃, respectively. Due to the proximity of the Curie transition of Gd and some of Gd-based intermetallics, it is possible to make composite materials, which allow the extension of the working temperature span of Gd though at the expense of a reduced response (Gębara *et al.*, 2020; Law *et al.*, 2016). Although the overlap of different second-order phase transitions prevents the collapse of the magnetocaloric magnitudes onto a single universal curve, the partial collapse of the Δs_{iso} curves in this type of composites allows the reconstruction and deconvolution of the individual magnetocaloric responses of the constituent phases (Díaz-García *et al.*, 2020). Having RE elements, RE₂Fe₁₇ alloys (crystallizing in the Th₂Zn₁₇-type structure) presents a much lower criticality due to the high content of Fe. For Nd₂Fe₁₇ alloy, remarkable responses of $\Delta s_{\text{iso}}^{\text{max}} = -3.1 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 1.9 \text{ K}$ for 2 T were attained at 323 K (Dan'kov *et al.*, 2000).

Two relevant examples of materials avoiding RE elements are AlFe₂B₂ and Mn₅Ge₃ alloys. For the AlFe₂B₂ case, it underwent a Curie transition at 272 K with associated values of $\Delta s_{\text{iso}}^{\text{max}} = -2.7 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 1.2 \text{ K}$ for 2 T (Barua *et al.*, 2019; Tan *et al.*, 2013). The second-order character of this system is corroborated by their good scaling behavior (Lamichhane *et al.*, 2018). However, it shows certain magnetoelastic coupling (Lewis *et al.*, 2015) and its nature is still under investigation (Lejeune *et al.*, 2021). The response of this system could be two-fold increased to $\Delta s_{\text{iso}}^{\text{max}} = -6.5 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 2.2 \text{ K}$ by adding small amounts of Ga and Ge (Barua *et al.*, 2019). The Mn₅Ge₃ system showed a magnetocaloric response of $\Delta s_{\text{iso}}^{\text{max}} = -3.9 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 1.8 \text{ K}$ for 2 T at 297 K (Toliński and Synoradzki, 2014) following the scaling behavior, thus corresponds to a second order phase transition (Zheng *et al.*, 2013).

For some well-known first-order magnetocaloric materials, which will be further discussed later, it is possible to tune the response to a second-order one by either changing the order of the transition, as in magnetoelastic type materials, or displacing (or suppressing) the first-order transition far from the second-order one in magnetostructural type materials. As a representative example of the former class, Co-doping in La(Fe,Si)₁₃ alloys is able to tune the typical magnetoelastic first-order transition at 200 K to a second-order one at room temperature. 7–8 at. % of Co and Si led to $\Delta s_{\text{iso}}^{\text{max}}$ (2 T) = $-8.7 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}$ (1.9 T) = 3.3 K at around 290 K (Pulko *et al.*, 2015). Similar behavior is found for the (Mn,Fe)₂(P,Si) system by adjusting Mn:Fe and P:Si ratios (Dung *et al.*, 2011). Regarding materials that show magnetostructural transitions, Ga doping (≈ 11 at%) to the Gd₅(Si,Ge)₄ system gave a second-order response around room temperature with $\Delta s_{\text{iso}}^{\text{max}} = -3.8 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 3.6 \text{ K}$ at 295 K for 2 T (Palacios *et al.*, 2010). In the case of Heusler alloys, another typical example of materials undergoing magnetostructural transformation, the Ni₂Mn_{1.4}In_{0.6} composition exhibited a second-order response with $\Delta s_{\text{iso}}^{\text{max}} = -3.3 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 2.0 \text{ K}$ at around 317 K for 2 T (Singh *et al.*, 2016). The recently discovered all-d-metal Heusler alloy Ni₃₃Co₁₇Mn₃₀Ti₂₀ showed a second-order response with $\Delta s_{\text{iso}}^{\text{max}}$ (2 T) = $-1.5 \text{ J kg}^{-1} \text{ K}^{-1}$ at 273 K (Zhang *et al.*,



Fig. 2 Bubble chart indicating the supply risk index for most common raw materials employed for the fabrication of magnetocaloric material (Index > 1 identifies the material as critical). Data extracted from European Commission, Directorate-General for Internal Market Entrepreneurship and SMEs (Industry), Blengini, G., *et al.*, 2020. Study on the EU's list of critical raw materials (2020): Final report. Publications Office. Available at: <https://doi.org/10.2873/11619>.

2022b). In both cases of Heusler alloys, the magnetostructural transition, martensitic type, is suppressed. Regarding the interesting MnTX family of compounds, which is known to show a magnetostructural transformation, Cu doping of ≈ 2.3 at% in MnCoGe alloys leads to a second-order response of $\Delta S_{\text{iso}}^{\text{max}}(1 \text{ T}) = -8.7 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}(1 \text{ T}) = 1.0 \text{ K}$ at 304 K, decoupling the magnetostructural transition that is shifted to 500 K (Liu *et al.*, 2020).

For cryogenic applications in the range of 20–80 K, useful for hydrogen liquefaction applications, most of the compositions contain rare earths due to the large magnetic moment and the low temperature transitions that they present. The criticality of these materials is reduced by mixing the rare earths with abundant elements; however, finding the proper balance between criticality and performance is still an uphill challenge. Excellent responses are observed for RE-based Laves phases, having REX_2 composition that can crystallize in the hexagonal MgZn_2 and MgNi_2 or cubic MgCu_2 -type structures. This family of compounds can undergo either first- or second-order transitions. Selecting the p-block element Al as X, DyAl_2 and ErAl_2 Laves phases underwent second-order transitions at 64 and 13.5 K, respectively, covering the desired temperature range (von Ranke *et al.*, 1998). For DyAl_2 , magnetocaloric responses of $\Delta S_{\text{iso}}^{\text{max}} = -9.7 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 3.7 \text{ K}$ were achieved for 2 T. Regarding ErAl_2 , higher responses of $\Delta S_{\text{iso}}^{\text{max}} = -23 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 5.7 \text{ K}$ were observed for 2 T. Selecting X as a transition metal element, an interesting second-order response was found for RENi_2 Laves phases, among which GdNi_2 , DyNi_2 and HoNi_2 cases showed especially high values at 72.2, 21.0 and 13.2 K, respectively. For the GdNi_2 case, $\Delta S_{\text{iso}}^{\text{max}} = -5.9 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 2.3 \text{ K}$ for 2 T were observed (Taskaev *et al.*, 2020). For the Dy containing one, $\Delta S_{\text{iso}}^{\text{max}} = -11 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 3.8 \text{ K}$ were obtained for 2 T (Ćwik *et al.*, 2017). Finally, for the HoNi_2 case, $-14.6 \text{ J kg}^{-1} \text{ K}^{-1}$ and 4.6 K values were achieved for the same field (Ćwik *et al.*, 2018). For these materials, the lower the transition temperature, the higher the magnetocaloric effect.

In addition to Laves phases, a particular case is the HoB_2 compound (hexagonal AlB_2 structure), which has recently been discovered by employing machine learning tools (Castro *et al.*, 2020). The transition temperature of 15 K is near hydrogen liquefaction, showing competitive maximum values of $\Delta S_{\text{iso}}^{\text{max}} = -24.1 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 6.0 \text{ K}$ (for 2 T). RE-containing

ternary intermetallic alloys also show interesting responses for cryogenic applications. DyFeSi and ErFeSi (tetragonal CeFeSi-type structure) show transition temperatures of 70 and 25 K, respectively (Zhang *et al.*, 2013a,b). At these temperatures, the $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T})$ are -9.2 and $-13\text{ J kg}^{-1}\text{ K}^{-1}$ while $\Delta T_{\text{ad}}^{\text{max}}(2\text{ T})$ are 3.4 and 2.9 K for Dy- and Er-containing alloys, respectively. Similarly, GdNiAl and HoNiAl compositions (hexagonal ZrNiAl-type structure) show a remarkable magnetocaloric effect at 57 and 14 K, respectively, with peak values of $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T})$ of -5.2 and $-12.3\text{ J kg}^{-1}\text{ K}^{-1}$, respectively (Klimczak and Talik, 2010; Singh *et al.*, 2007). For HoNiAl, a maximum $\Delta T_{\text{ad}}^{\text{max}}(2\text{ T})$ of 4.1 K is found. It should be noted that even for cryogenic studies, in which the temperature span is physically very limited below the transition, the universal magnetocaloric construction works satisfactorily even for high magnetic field changes (up to 7 T), as shown in Fig. 3 for a series of RENiGa₂ alloys with transition temperatures ranging from 12 to 42 K (Guo *et al.*, 2022).

Amorphous alloys offer a versatile way for mixing rare earths with abundant elements in a single-phase state. Among those alloys having magnetocaloric effects falling in the cryogenic range, we highlight some recent studies on DyHoErCoAl (Huo *et al.*, 2015), GdHoErNiAl (Sheng *et al.*, 2018) and GdTbCoAl (Xue *et al.*, 2019) showing Curie transitions at 18, 25 and 73 K, respectively. The corresponding $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T})$ values of these systems were -5.5 , -4.0 and $-4.6\text{ J kg}^{-1}\text{ K}^{-1}$, for which the adiabatic temperature change data was not reported.

Regarding RE-free compound, MnSi showed a Curie transition at 33 K with peak values of $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T}) = -2.2\text{ J kg}^{-1}\text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}(2\text{ T}) = 2.6\text{ K}$ (Arora *et al.*, 2007). This compound crystallizes in the cubic B-20 structure, showing a helimagnetic character below the transition temperature. Although this system shows evidence of a second-order type transition, weak indications of a first-order character for low fields can be inferred (Samatham and Ganesan, 2017).

First-Order Magnetocaloric Materials

Magnetoelastic transitions

Linked to the magnetization evolution, these transitions involve moderate volume changes without the modification of the crystal structure. The magnetoelastic character is shown to be highly tunable, affecting the nature of the transition and, therefore, its hysteresis and magnetocaloric effect. FeRh alloy (CsCl-type structure) was the first material found to show giant magnetocaloric values around room temperature (Annaorazov *et al.*, 1996). However, the high criticality of Rh prevents this alloy to be considered for magnetic refrigeration applications. Nevertheless, this system shows a rather interesting magnetocaloric response with the highest $\Delta T_{\text{ad}}^{\text{max}}$ values to date, reaching up to -12.5 K for 2 T, reported from heat capacity measurements (Annaorazov *et al.*, 1992). Other studies show -9.2 K for 1.9 T by direct methods, having an $\Delta S_{\text{iso}}^{\text{max}}$ of $14\text{ J kg}^{-1}\text{ K}^{-1}$ for 2 T (Chirkova *et al.*, 2016). The outstanding magnetocaloric response of FeRh is associated with an antiferromagnetic (AF) to FM transition at 325 K upon heating, which is found to be significantly affected by microstructure and secondary phases (Chirkova *et al.*, 2017). Although the associated thermal hysteresis is about 8 K, a large cyclic response of $\Delta T_{\text{ad}}^{\text{max}} = -6\text{ K}$ (for 1.9 T) is reported. This is due to the significant evolution of the transition with field, -8.5 K/T , which enables the suppression of the thermal hysteresis effects at moderate fields (Chirkova *et al.*, 2016). Basic research in this system is still of interest as revealed by a recent literature survey on the current research trends in magnetocaloric materials during 2019 - 2022 (Law *et al.*, 2022).

The family of La(Fe,Si)₁₃ intermetallic alloys, already referred in previous section, crystallizes in the NaZn₁₃-type structure and shows remarkable responses due to a magnetoelastic FM to PM transition upon heating while it is mostly based on abundant elements. Si addition is needed for stabilizing the NaZn₁₃-type phase (Krypiakewytch *et al.*, 1968). The transition temperature is around 200 K but it can be tuned to room temperature by the addition of different elements. As previously discussed, Co additions shift the transition to room temperature but at the expense of changing its character to a second-order type (Bjork *et al.*, 2010a;

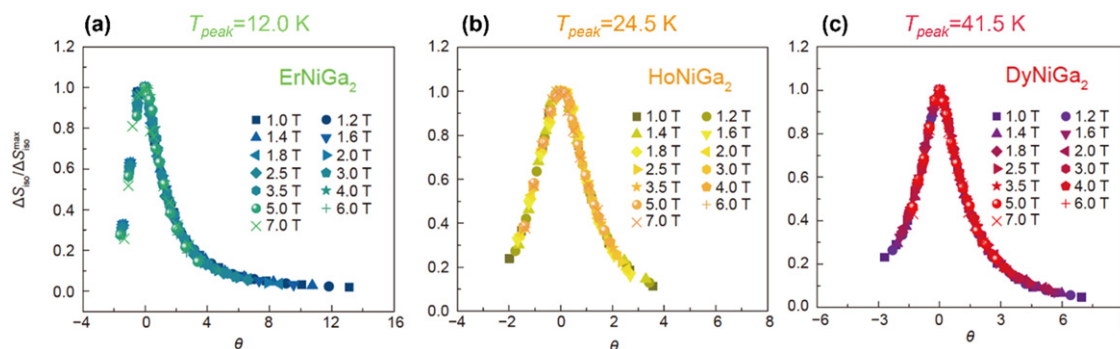


Fig. 3 Universal scaling of the isothermal entropy change for (a) ErNiGa₂, (b) HoNiGa₂ and (c) DyNiGa₂ compounds. Adapted from Guo, D., Moreno-Ramírez, L.M., Law, J.-Y., Zhang, Y., Franco, V., 2022. Excellent cryogenic magnetocaloric properties in heavy rare-earth based HRENiGa₂ (HRE = Dy, Ho, or Er) compounds. *Sci China Mater.* Available at: <https://doi.org/10.1007/s40843-022-2095-6>, which is under open access Creative Commons CC BY license.

Katter *et al.*, 2008). Other dopants, such as Si and Ni, can also increase the transition temperature although they do not yield competitive responses when approaching room temperature (Franco *et al.*, 2017; Moreno-Ramírez *et al.*, 2018b). When using Mn as a dopant, the transition temperature is decreased at a rate of -20 K per at. % (Krautz *et al.*, 2014). Cr doping also decreases the transition temperatures of the La(Fe,Si)_{13} alloys but their magnetocaloric responses evolve in a non-monotonic way: the first-order character of the transition and performance increase for low Cr concentrations while the opposite occurs with large Cr content (Moreno-Ramírez *et al.*, 2019b). It is also possible to increase the first-order character with La substitution by Pr or Nd (Davarpanah *et al.*, 2021) or by applying pressure (Hao *et al.*, 2020a; Karpenkov *et al.*, 2020). However, the most extended compositional modification is hydrogenation as it enables the tuning of the transition to room temperature while keeping the first-order character and large magnetocaloric response (Fujita *et al.*, 2003). However, hydrogenation causes decrepitation of the material (Liu *et al.*, 2012a) and, therefore, additional steps, such as additive manufacturing for shaping and avoiding corrosion, are needed (Díaz-García *et al.*, 2022). Hydrogenation leads to a response of $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T}) = -20\text{ J kg}^{-1}\text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}(2\text{ T}) = 7\text{ K}$ slightly above room temperature (330 K for 11 at. % Si content) with a thermal hysteresis of $\sim 3\text{--}4\text{ K}$ (Fujita *et al.*, 2003; Moreno-Ramírez *et al.*, 2022).

Analogously to the previous case, the $(\text{Mn,Fe})_2(\text{P,Si})$ family shows a remarkable magnetocaloric effect arising from a FM to PM magnetoelastic transition with increasing temperature while based on abundant elements. It should be noted that, depending on the composition, this system can also show magnetostructural transformations (not covered here) (Dung *et al.*, 2011). $(\text{Mn,Fe})_2(\text{P,Si})$ alloys crystallize in a hexagonal Fe_2P -type structure in which the cell volume is modified along the c -axis with the transformation (Guillou *et al.*, 2014a). Apart from the usual P substitution by Si, other elements, such as As and Ge, can be employed for tuning the response of this system (Brück *et al.*, 2005; Dagula *et al.*, 2005). Sticking to Si dopant, $\text{MnFeP}_{0.50}\text{Si}_{0.50}$ composition shows a large magnetocaloric response with a maximum $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T}) = -30\text{ J kg}^{-1}\text{ K}^{-1}$ for 2 T around 300 K while showing a large thermal hysteresis of 35 K (Cam Thanh *et al.*, 2008). This hysteresis can be reduced by adjusting the Mn:Fe ratio. For the $\text{Mn}_x\text{Fe}_{1.95-x}\text{P}_{0.50}\text{Si}_{0.50}$ series, a hysteresis of 5, 2 and 1 K are obtained for Mn contents of 1.20, 1.25 and 1.30, respectively (Dung *et al.*, 2011). However, this decrease of hysteresis is accompanied by a drastic decrease of the magnetocaloric effect due to the reduction of the first-order character of the transition. Finer tuning can be performed by small B additions, leading to negligible values of the hysteresis in comparison to the undoped sample. $\text{MnFe}_{0.95}\text{P}_{0.585}\text{Si}_{0.34}\text{B}_{0.075}$ composition leads to $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T}) = 17.6\text{ J kg}^{-1}\text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}(1\text{ T}) = 2.5\text{ K}$ at 290.5 K (Guillou *et al.*, 2014a). For 2 T, a maximum temperature change under cyclic conditions of 4.3 K has been reported (Gottschall *et al.*, 2019b). Furthermore, the complexity of reducing secondary phases and the appearance of virgin effects in this family of compounds is a cause of concern (Fries *et al.*, 2017). Recently, it has been shown that V doping can lead to further reduced thermal hysteresis (Lai *et al.*, 2023).

For cryogenic applications, rare earth Laves phases, previously introduced, are extensively studied. In the case of RECo_2 (RE = Ho, Er), FM to PM magnetoelastic transitions take place at 82 and 32 K, respectively. For the ErCo_2 case, the magnetocaloric effects are reported as $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T}) = 35\text{ J kg}^{-1}\text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}(2\text{ T}) = 3.7\text{ K}$ with a thermal hysteresis of $\sim 2\text{ K}$ (Wada *et al.*, 1999). For HoCo_2 alloy, the associated values are $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T}) = 19\text{ J kg}^{-1}\text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}(2\text{ T}) = 3.2\text{ K}$ with similar thermal hysteresis (Nikitin and Tishin, 1991; Sechovsky *et al.*, 2007). By mixing Ho and Er, it is possible to elaborate a series of compositions with transition temperatures that range from 32 to 82 K while keeping the good magnetocaloric properties (Zhu *et al.*, 2011). Recent work shows that Fe and Ni additions can further reduce the hysteresis of the RECo_2 (RE = Er, Ho) systems (by reducing the first-order character) while tuning the transitions to higher and lower temperatures, respectively. In this way, it will be possible to develop a composite material that covers the range of 20–80 K for hydrogen liquefaction applications without hysteresis (Tang *et al.*, 2022). Besides Laves phases, the RE_3X alloys, with Fe_3C -type structure, can exhibit magnetoelastic transitions with remarkable magnetocaloric responses at cryogenic temperatures. Ho_3Co and Dy_3Co , upon heating, undergo AF to FM transition at 21 and 44, respectively. Inverse magnetocaloric responses with $\Delta S_{\text{iso}}^{\text{max}}(5\text{ T}) = 14.5$ and $13.9\text{ J kg}^{-1}\text{ K}^{-1}$ are obtained, respectively (Shen *et al.*, 2010; Shen and Wu, 2011). For Gd_3Ru , maximum values of $-22.5\text{ J kg}^{-1}\text{ K}^{-1}$ and 3.7 K are obtained for 2 T at 56 K (Monteiro *et al.*, 2015), although criticality is much higher. Recently, RE_2In alloys (RE = Eu and Pr) have been shown to be potential magnetocaloric materials with a magnetoelastic transition of negligible hysteresis (0.1 K) despite being associated with large latent heat (Biswas *et al.*, 2020; Guillou *et al.*, 2018). They crystallize in the Co_2Si -type structure, in which magnetocaloric responses as large as $\Delta S_{\text{iso}}^{\text{max}} = -28\text{ J kg}^{-1}\text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}} = 5.0\text{ K}$ for 2 T at 56 K are reported for Eu_2In . For Pr_2In , $\Delta S_{\text{iso}}^{\text{max}} = -15\text{ J kg}^{-1}\text{ K}^{-1}$ is obtained for 2 T at 57 K. For both compositions, their large performances fall within the range of interest for hydrogen liquefaction.

Regarding non-RE-based compositions, CoS(Se)_2 alloys present a tunable magnetocaloric effect in the range from 30 to 120 K with maximum values of $3 - 7\text{ J kg}^{-1}\text{ K}^{-1}$ for 1 T (Wada *et al.*, 2006). There have also been attempts to tune the magnetocaloric effects of La(Fe,Si)_{13} and $(\text{Mn,Fe})_2(\text{P,Si})$ systems down to cryogenic levels. For the former, it is possible to achieve a remarkable magnetocaloric effect in the desired range of 20–80 K with $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T}) = -9.5\text{ J kg}^{-1}\text{ K}^{-1}$ at 78 K and $\Delta S_{\text{iso}}^{\text{max}}(2\text{ T}) = -5.5\text{ J kg}^{-1}\text{ K}^{-1}$ at 48 K for $\text{La}_{0.69}\text{Ce}_{0.31}\text{Mn}_{0.34}\text{Fe}_{1.0.96}\text{Si}_{1.7}$ and $\text{La}_{0.66}\text{Ce}_{0.34}\text{Mn}_{0.40}\text{Fe}_{1.0.90}\text{Si}_{1.7}$, respectively (Lai *et al.*, 2021). For the $(\text{Mn,Fe})_2(\text{P,Si})$ system, aided by machine learning tools and using Co as the dopant, a value of $\Delta S_{\text{iso}}^{\text{max}} = -3.7\text{ J kg}^{-1}\text{ K}^{-1}$ for 2 T at 77 K is achieved while $\Delta T_{\text{ad}}^{\text{max}}$ is reported to be 1.4 K for 5 T (Lai *et al.*, 2022).

As shown, element doping followed by the alteration of the first-order character is currently the most efficient strategy for reducing hysteresis and, therefore, to obtain improved reversible/cyclic performances. Hence, the search for the critical composition in magnetocaloric materials (where their first-order phase transition crossovers to second-order), which is possible for those with a magnetoelastic transition, is crucial for performance optimization (Sandeman, 2012). In this case, exponent n analyses are a useful tool since they can identify the critical compositional point with a quantitative magnitude (Franco *et al.*, 2017; Law *et al.*, 2018). As an example, the optimization process of the magnetocaloric response through tuning the first-order character in hydrogenated La(Fe,Si)_{13} is illustrated in Fig. 4. For this study, Mn is employed as a dopant, which could reduce hysteresis but, undesirably, degrades the magnetocaloric response (both cooling and heating branches) as shown in panel a of Fig. 4. However,

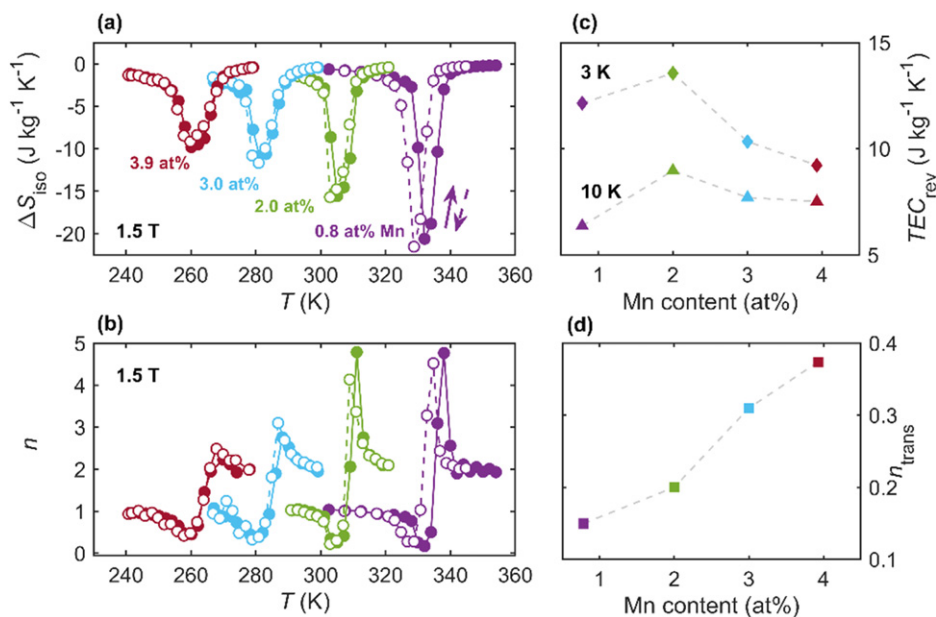


Fig. 4 Temperature dependences of the isothermal entropy change (a) and the exponent n (b) for a series of Mn containing La(Fe,Si)₁₃H alloys. TEC magnitude of the reversible response using 3 and 10 K temperature lift (c). Exponent n at the transition for the series which indicates the gradual modification of the first-order character as Mn content increases (d). For further details, the reader is referred to Moreno-Ramírez, L.M., Law, J.Y., Borrego, J.M., et al., 2022. First order phase transition in high-performance La(Fe,Mn,Si)₁₃H despite negligible hysteresis. Under review.

the cyclic response is optimized as depicted in the TEC_{rev} magnitude (using 3 and 10 K for T_{lift}), plotted in **panel c**. According to both TEC_{rev} curves, the composition with the largest reversible response is the one with 2 at% Mn. However, the compositional range where the maximum possible cyclic response is achieved is fairly narrow (0.8–3 at% of Mn), requiring fine analysis tools. Among the different methods, the exponent n analysis is reported to be more precise than the traditional ones, such as Mössbauer spectroscopy and the Barerjee's criterion (Moreno-Ramírez et al., 2022, 2018b). A magnetic first-order phase transition will show an overshoot of exponent n above 2 around the transition temperature (Law et al., 2018), while the signature of a material with the critical composition is given by exponent n values of 0.4 at the transition temperature (Franco et al., 2017). Considering this, exponent n curves in **panel b** show the characteristic overshoot of $n > 2$ of first-order phase transitions. The monotonic decrease of the overshoot values with increasing Mn content indicates that Mn is gradually reducing the first-order character of the transition. However, the exponent n below 0.4 for all the compositions reveals that the critical composition is not reached (**panel d**). Extrapolating the results, a critical Mn content of 4.1(1) at% can be estimated. It should be highlighted that hysteresis is not only affected by the nature or characteristics of the transition, but also by extrinsic factors, such as sample size, shape, and stress, which should also be accounted for during the performance analysis (Moore et al., 2009).

Magnetostructural transitions

These transitions can be understood as solid–solid first-order phase transitions that occur between two structures with different magnetizations. The larger the magnetization difference, the larger the effect produced by magnetic fields on the transformation. Due to large volume changes involved in magnetostructural transitions and the subsequently large latent heat, they give rise to the largest found ΔS_{iso} values among thermomagnetic phase transitions. However, this also leads to drawbacks, such as the reduced ΔT_{ad} values or large thermal hysteresis in comparison to magnetoelastic samples. The first magnetostructural material considered here is Gd₅Si₂Ge₂ as it has driven the magnetocaloric research since the nineties. The transition in Gd₅Si₂Ge₂ occurs between FM orthorhombic and PM monoclinic structures (Gd₅Si₂Ge₂ and Gd₅Si₄ types, respectively), leading to a magnetocaloric effect with maximum values of $\Delta S_{iso}^{max} = -14 \text{ J kg}^{-1} \text{K}^{-1}$ and $\Delta T_{ad}^{max} = 7.4 \text{ K}$ for 2 T at 276 K (Pecharsky and Gschneidner, 1997a). These first reported values can be increased around 50% by employing high purity Gd and optimized thermal treatments (Pecharsky et al., 2003). Besides their large magnetocaloric values, a hysteresis of about 5 K is also observed. In cyclic conditions, the reversible ΔT_{ad} is 4.9 K, although without degradation of the transition or hysteresis (Biswas et al., 2019a). Fe doping leads to reduced hysteresis but at the expense of a significantly lowered response (Provenzano et al., 2004). Modifying the Si:Ge ratio, a tunable transition in the range of 20–300 K is achieved (Pecharsky and Gschneidner, 1997b). The main issue with this system is its high material criticality, owing to the presence of Gd and Ge.

Looking for transition metal-based materials, intermetallic Heusler alloys with XYZ or X₂YZ stoichiometry (half or full Heusler, respectively) are extensively studied. Typically, sites X and Y are transition metal elements and Z is an element of III–VA group of the periodic table. The out-of-stoichiometry Ni₂Mn–Z (Z = Ga, In, Sn and Sb) family of full Heusler alloys includes the paradigmatic examples for magnetocalorics (Bachaga et al., 2019; Planes et al., 2007). These compositions show a magnetostructural

transformation between cubic FM and tetragonal PM (or ferrimagnetic) structures (austenite and martensite, respectively). The low temperature martensitic structure can present modulation which favored the shape memory properties of these alloys (Gruner *et al.*, 2018). The largest magnetocaloric effect is observed for $Z = \text{In}$, being $\text{Ni}_{50.2}\text{Mn}_{35.0}\text{In}_{14.8}$ a representative case with $\Delta s_{\text{iso}}^{\text{max}}(2\text{ T}) = 23.5\text{ J kg}^{-1}\text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}(1.93\text{ T}) = -2.7\text{ K}$ at 302 K (Taubel *et al.*, 2018). By reaching a good geometric compatibility between austenite and martensite, a lowered hysteresis of 4 K can be achieved, which leads to a reversible response of 80 % of the maximum ($25\text{ J kg}^{-1}\text{ K}^{-1}$) for 6 T (Stern-Taulats *et al.*, 2014). Even though this is still regarded as a high magnetic field, geometric compatibility has demonstrated to be a beneficial method for minimizing hysteresis though additional systematic studies may be needed. For $Z = \text{Sn}$ samples, smaller values are obtained, $\Delta s_{\text{iso}}^{\text{max}}(2\text{ T}) = 11.3\text{ J kg}^{-1}\text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}(1.93\text{ T}) = -1.1\text{ K}$ at 300 K for $\text{Ni}_{51.2}\text{Mn}_{35.1}\text{Sn}_{13.7}$ sample (Taubel *et al.*, 2018). Replacing Ni by Co gives rise to a significant improvement of the response for both In- and Sn-containing systems. A large $\Delta T_{\text{ad}}(1.95\text{ T})$ of -8 K has been achieved for $\text{Ni}_{45.7}\text{Co}_{4.2}\text{Mn}_{36.6}\text{In}_{13.5}$ (Gottschall *et al.*, 2015). Despite showing a thermal hysteresis of 10 K, this composition shows a reversible response as high as 3 K due to the high field evolution of the transition (-8 K/T). For Sn-containing compositions, $\text{Ni}_{45.7}\text{Co}_{4.9}\text{Mn}_{37.9}\text{Sn}_{11.5}$ presents $\Delta s_{\text{iso}}^{\text{max}}(2\text{ T}) = 23.7\text{ J kg}^{-1}\text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}(1.93\text{ T}) = -2.6\text{ K}$ at around 330 K with a thermal hysteresis of 5 K (Taubel *et al.*, 2018). An additional aspect that should be highlighted is that substantial volume changes related to first-order phase transitions often result in a loss of the samples' structural cohesiveness when they are subjected to cyclic experiments, which in turn affects their magnetocaloric responses. In this regard, all-d metal Ni(Co)-Mn-Ti Heusler alloys show improved mechanical properties (Wei *et al.*, 2019). Partial Ni substitution by Co or Fe are needed to enhance magnetization changes during the transformation, although Fe is shown to be less effective (Zeng *et al.*, 2019). A tunable response around room temperature is achieved by modifying Ni:Co and Mn:Ti ratios. The maximum reported values for this series are $\Delta s_{\text{iso}}^{\text{max}}(2\text{ T}) = 34\text{ J kg}^{-1}\text{ K}^{-1}$ and $\Delta T_{\text{ad}}^{\text{max}}(1.9\text{ T}) = -3.5\text{ K}$ at 250 K upon heating for the $\text{Ni}_{37}\text{Co}_{13}\text{Mn}_{34}\text{Ti}_{16}$ composition. For room temperature transitions, the maximum reported values are around $20\text{ J kg}^{-1}\text{ K}^{-1}$. However, the cyclic response of this system is limited to not more than 0.5 K due to a thermal hysteresis of 10 K coupled with a weak evolution of the transition with field ($\sim -2\text{ K/T}$) (Taubel *et al.*, 2020). The inverse magnetocaloric effect of these materials, with the opposite sign of that of Curie transitions, can lead to competing and compensated magnetocaloric responses in cases where the first-order martensitic transition and the Curie transition of the austenitic phase overlap within the same temperature range. It has been demonstrated that the exponent n analysis can correctly identify first-order transformations even when closely overlapped with a second-order response that strongly contributes to the overall magnetocaloric response (Law *et al.*, 2019). Even in cases of apparently low overlap, the second-order Curie transition can have a significant detracting effect from the targeted inverse response of the martensitic transformation. To facilitate material optimization, the scaling of the Δs_{iso} response of the Curie transition has been used to deconvolute the martensitic response from the overall response of a multiphase system (Díaz-García *et al.*, 2021a).

MnTX systems ($T = \text{TM}$ element as Co, Ni and $X = \text{p-block}$ element as Si or Ge) can show magnetostructural transformation from orthorhombic (TiNiSi-type) to hexagonal (Ni_2In -type) structures with increasing temperature. Employing Co as a second transition metal and Ge as p-block element, the equiatomic MnCoGe alloy undergoes the orthorhombic to hexagonal transformation at around 650 K without significant magnetization evolution (PM to PM) as the Curie of the orthorhombic structure is around 335 K (Kanomata *et al.*, 1995). Different compositional modifications have been investigated to tune the first-order transition to room temperature while promoting a significant magnetization change. Minor B additions tune the transition to around 275 and 304 K with a significant magnetization difference of $50\text{ A m}^2\text{ kg}^{-1}$ between FM orthorhombic and PM hexagonal structures (Aznar *et al.*, 2019). $\Delta s_{\text{iso}}^{\text{max}}$ values around $-20\text{ J kg}^{-1}\text{ K}^{-1}$ for 2 T are obtained for the MnCoGeB_{0.03} alloy. Its thermal hysteresis spans in the range 10–15 K. Another strategy for performance optimization in MnTX is to replace Mn by Cu, which tuned the response to around room temperature: Mn_{0.915}Cu_{0.085}CoGe showed $\Delta s_{\text{iso}}^{\text{max}}(2\text{ T}) = -20.3\text{ J kg}^{-1}\text{ K}^{-1}$ ($-52.5\text{ J kg}^{-1}\text{ K}^{-1}$ for 5 T) at 304 K with similar hysteresis values as previous alloys (Samanta *et al.*, 2012). Regarding ΔT_{ad} , a maximum value of 1.5 K has been determined by direct methods at 1.9 T for MnCo_{0.95}Ge_{0.95} (Liu *et al.*, 2012b). Other interesting MnTX composition include MnNiSi, which undergoes a structural phase transition at temperatures as high as 1200 K (being both phases in the PM state) (Bažela *et al.*, 1981). To lower the transition of MnNiSi to room temperature, an effective approach is the isostructural alloying with certain compositions, such as FeCoGe (Samanta *et al.*, 2015) or Fe₂Ge (Zhang *et al.*, 2015), which presents stable hexagonal Ni_2In -type structure. Focusing on the latter (due to the absence of Co, a critical element), a tunable magnetocaloric effect in the range of 200–500 K is achieved. In particular, the $(\text{NiMnSi})_{0.66}(\text{Fe}_2\text{Ge})_{0.34}$ composition is reported to show a significant value of $\Delta s_{\text{iso}}^{\text{max}} = -30\text{ J kg}^{-1}\text{ K}^{-1}$ for 2 T around room temperature ($\approx -50\text{ J kg}^{-1}\text{ K}^{-1}$ for 5 T) (Zhang *et al.*, 2015). These high Δs_{iso} values are ascribed to the large latent heat accompanying the transition; however, the field-induced transition is far from saturation values for 5 T. Thermal hysteresis around 15 K is observed, leading to reduced cyclic responses ($-3\text{ J kg}^{-1}\text{ K}^{-1}$ for 5 T in $(\text{NiMnSi})_{0.66}(\text{Fe}_2\text{Ge})_{0.34}$), which is very detrimental for the applicability of the system. In this composition, $\Delta T_{\text{ad}}^{\text{max}}$ is found to be 1.8 K for 1.75 T, but pulverization of the alloy, which occurs naturally with repeated transformations, reduces it by 40 % (Moreno-Ramírez *et al.*, 2021). As Al is more abundant and cheaper than Ge, it is used as a complete replacement of Ge in MTX alloys, retaining the significant magnetocaloric properties, although it does have the drawbacks previously mentioned (Biswas *et al.*, 2019b). For Mn_{0.5}Fe_{0.5}NiSi_{0.45}Al_{0.055}, a response of $-20\text{ J kg}^{-1}\text{ K}^{-1}$ is reported but the associated hysteresis increases to $\sim 25\text{ K}$. It remains a challenge to reduce the hysteresis in this MnTX systems. One possibility is to improve the geometric compatibility between the orthorhombic and hexagonal structures in the MnNiGe alloy, by which its hysteresis decreases from 25 to 5 K for the Mn_{0.9}Fe_{0.2}Ni_{0.9}Ge_{0.95}Si_{0.05} composition, at the same time, offering a reversible response of $22\text{ J kg}^{-1}\text{ K}^{-1}$ for 5 T at 271 K (Liu *et al.*, 2019).

In this material system, cryogenic applications are less reported because such low temperatures cause structural transitions to occur less readily. Among the few reports of materials undergoing magnetostructural transformation in the cryogenic range, Gd₅Sn₄ stands out because non-critical Sn is employed. It transforms from Gd₅Si₄ to Gd₅Ge₄-type structure at 82 K upon heating,

yielding a $\Delta S_{\text{iso}}^{\text{max}} (\sim 3 \text{ T}) = -33 \text{ J kg}^{-1} \text{ K}^{-1}$ (Ryan *et al.*, 2003). On cooling, the transformation does not complete even at 20 K likely due to the slow kinetics (Wang *et al.*, 2004).

In this type of materials, the larger the latent heat, the larger the entropy change during the transition, ΔS_{trans} . However, considering the Clausius-Clapeyron equation for describing ideal first-order transitions:

$$\frac{dT_{\text{trans}}}{dH} = \frac{\Delta M_{\text{trans}}}{\Delta S_{\text{trans}}}, \quad (10)$$

it is evident that as the ΔS_{trans} increases the evolution of the transition temperature with field (dT_{trans}/dH) decreases. Typically, this reduction also leads to lowered ΔT_{ad} values. This can be solved by either increasing the magnetization jump of the transition (ΔM_{trans}) or decreasing the associated latent heat to decrease ΔS_{trans} . It is worth noting that the latter appears to be an ineffective strategy given that it can lead to lower ΔS_{iso} values. For obtaining $\Delta S_{\text{iso}} \approx \Delta S_{\text{trans}}$, the transformation must be completely driven by the applied magnetic field, which is unlikely to be achieved with moderate fields up to 2 T. Therefore, lowering the latent heat does not necessarily produce a lower ΔS_{iso} for moderate magnetic fields that do not complete the transformation. As an example, for a Ni(Co)Mn(Fe)Ti series, it can be observed that $\Delta S_{\text{iso}} (2 \text{ T})$ is significantly improved with Fe additions (panel a of Fig. 5) while the DSC scans show a decreased contribution of the lattice (panel b) (Khan *et al.*, 2023). Overall, the main effect of Fe addition is to decrease the latent heat of the transition while retaining the magnitude of the magnetization difference between martensite and austenite (panel c). Besides the enhanced $\Delta S_{\text{iso}} (2 \text{ T})$, the field evolution of the transition (panel d) shows a two-fold increase, which leads to broader peaks (and probably larger ΔT_{ad} , which is under investigation).

Materials Comparison

In order to illustrate and sum up the performance comparison of previously mentioned materials, Fig. 6 shows the first shot (i.e., non cyclic) $|\Delta S_{\text{iso}}^{\text{max}}|$ vs. $|\Delta T_{\text{ad}}^{\text{max}}|$ data of representative examples of each material family according to the range of applicability, either room temperature (panel a) or cryogenic (panel b), respectively. For room temperature applications, the magnetocaloric responses of Gd (green dashed lines) are highlighted for performance comparison. Among the second-order materials, Gd shows the highest $|\Delta T_{\text{ad}}^{\text{max}}|$, while those showing some magnetoelastic characteristics surpass the $|\Delta S_{\text{iso}}^{\text{max}}|$ of Gd, e.g., second-order La(Fe, Co, Si)₁₃ or doped AlFe₂B₂. Several first-order materials, while their first shot responses clearly surpass $|\Delta T_{\text{ad}}^{\text{max}}|$ of Gd, they exhibit significant hysteresis. However, when the reversible responses of first-order materials are taken into account, only FeRh outperforms the magnetocaloric response of Gd. Magnetoelastic materials with compositions close to the critical point for both La(Fe, Mn, Si)₁₃-H and (Mn, Fe)₂(P, Si, B) alloys exhibit ΔS_{iso} values that overshadow Gd's while their ΔT_{ad} data are marginally below those of Gd. Overall, the highest values of $|\Delta S_{\text{iso}}^{\text{max}}|$ are found in magnetostructural materials, however, even for the first-shot characterization, they do not exhibit good ΔT_{ad} performance. According to the panel b of Fig. 6, second-order materials exhibit a

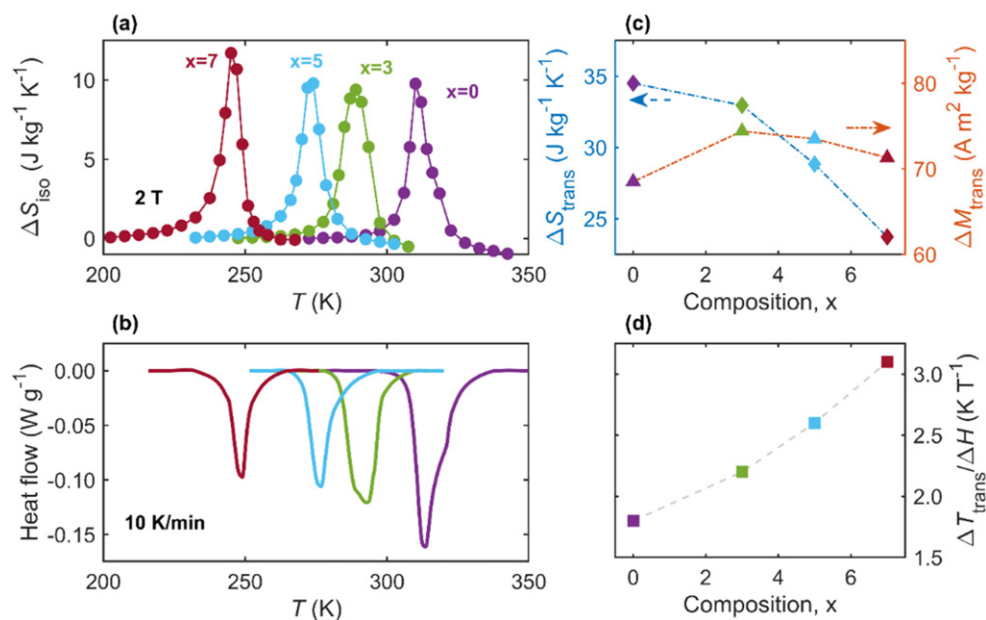


Fig. 5 Temperature dependence of the isothermal entropy change (a) and DSC scans (b) for a series of Ni₃₆Co₁₄Mn_{35-x}Fe_xTi₁₅. Transition entropy change and magnetization change for the martensitic transition for the series (c). Field evolution of the martensitic transition temperature as a function of the Fe content (d). For further details, the reader is referred to Khan, A.N., Moreno-Ramírez, L.M., Díaz-García, Á., Law, J.Y., Franco, V., 2023. All-d-metal Ni(Co)-Mn(X)-Ti (X = Fe or Cr) Heusler alloys: Enhanced magnetocaloric effect for moderate magnetic fields. *J. Alloy. Compd.* 931, 167559. Available at: <https://doi.org/10.1016/j.jallcom.2022.167559>.

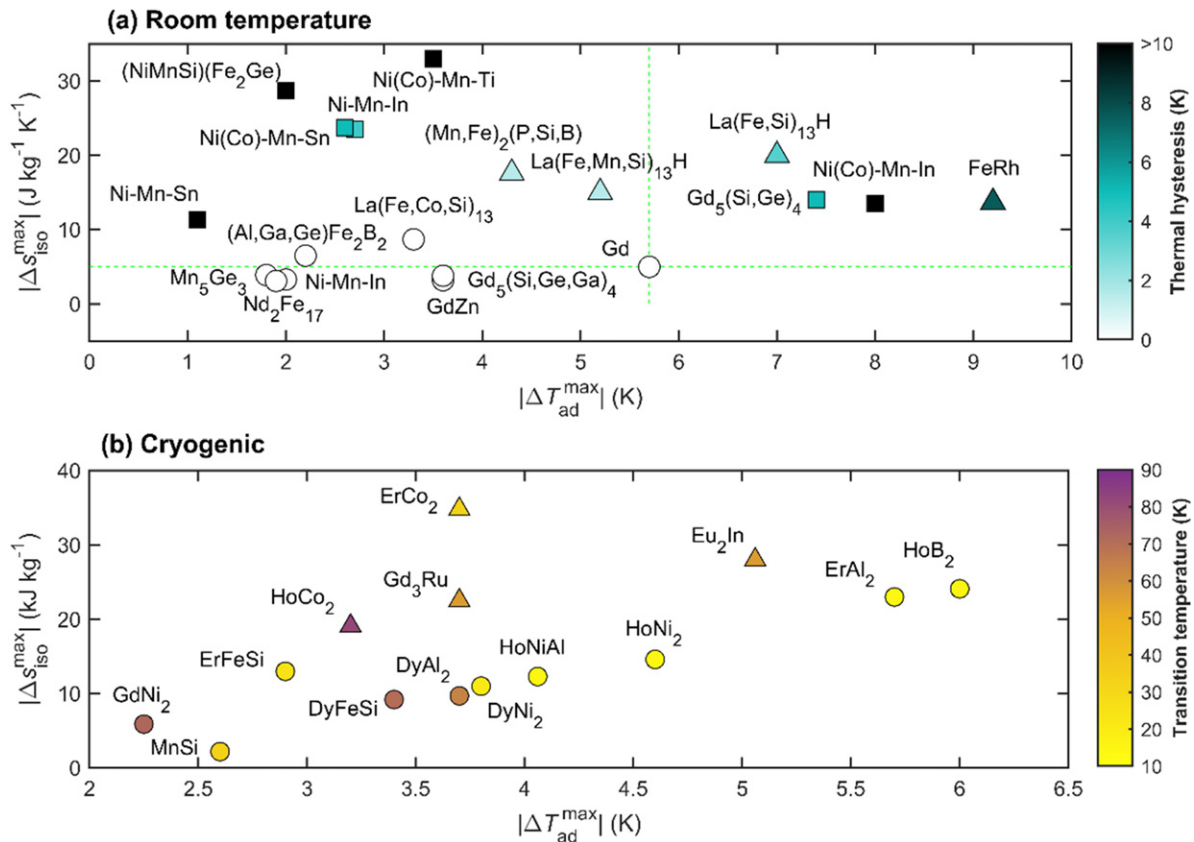


Fig. 6 $|\Delta S_{\text{iso}}^{\text{max}}|$ vs. $|\Delta T_{\text{ad}}^{\text{max}}|$ for 2 T for the representative magnetocaloric materials of each family for room temperature (a) and cryogenic applications (b). The type of the phase transition is indicated by the symbol (circles for second-order while triangles and squares for magnetoelastic and magnetostructural first-order, respectively). Color indicates hysteresis for panel a while that of panel b indicates the transition temperature. For some ΔT_{ad} data taken from the literature, their values for 1.9 T are employed instead of 2 T.

linear trend in the cryogenic region. On the other hand, the research trend for magnetoelastic materials is less obvious, though they show the highest $|\Delta S_{\text{iso}}^{\text{max}}|$ values in this temperature range. Still, they show lower $|\Delta T_{\text{ad}}^{\text{max}}|$ compared to second-order materials having similar transition temperatures (except for Eu_2In , which exhibits superior properties).

Future Perspectives

To advance the magnetocaloric technology, it is essential to both discover new materials and optimize existing ones (for example, by improving the geometric compatibility in magnetostructural transitions). In this regard, the use of machine learning tools in recent years has reduced the number of trial-and-error studies in the field of materials research. In these methods, a sizeable amount of material datasets can be analyzed to investigate the relationships among physical properties, complemented by first-principles calculations (Bocarsly *et al.*, 2017; Sanvito *et al.*, 2022; Schmidt *et al.*, 2019). They are based on predictive models among selected properties using statistical analyses from massive experimental data without specific programming. Recently, a few initiatives in magnetocaloric materials have yielded encouraging outcomes; some of them are already covered in this review. In one of them, machine learning analysis aids the discovery of HoB_2 to have a remarkable magnetocaloric effect at cryogenic temperatures (Castro *et al.*, 2020). For well-known magnetocaloric materials, machine learning makes it possible to exceed the current low-temperature limit of the $(\text{Mn,Fe})_2(\text{P,Si})$ system (Lai *et al.*, 2022) or correlate magnetocaloric responses to transition temperatures or hysteresis while tuning compositions for room temperature applications of $\text{La}(\text{Fe,Si})_{13}$ and manganite families (Owolabi *et al.*, 2016; Tu *et al.*, 2022; Zhang *et al.*, 2018).

Furthermore, a revolutionary concept for material design focuses on the central area of the multiprincipal elements phase diagram, which addresses the limitations of near-maturity conventional method of developing alloys. This new material design concept involves blending several principal elements for a large configuration entropy of mixing, rather than alloying elements to dilute one (or two) base constituent(s) as is the case with conventional alloys. These new alloys have been dubbed High-Entropy Alloys (HEAs), a catchy new name, by the community, and revealed to exhibit superior mechanical properties than conventional alloys. HEAs were initially restricted to five or more principal elements with equimolar concentrations for obtaining a single-phase metallic solid solution. Today, as more HEAs were reported, their definitions evolve to embracing less than five principal elements of non-equimolar compositions

with microstructures of any-type and any-number of phases, including intermetallic and ceramic compounds (for further information, readers are recommended to refer to references (Law and Franco (2021, 2022) and The Minerals Metals & Materials Society (TMS) (2021)). A broad compositional space is encompassed by the HEA concept, which offers lots of opportunities for exploring novel properties. This is very useful for designing new magnetocaloric materials with the aim of combining large magnetocaloric response with optimal mechanical properties, a prevailing concern in magnetocalorics for decades. Given the scarcity in the reports of functional HEAs (compared to those of structural HEAs), it is worthwhile to design magnetocaloric HEAs, especially since their performance is not usually competitive with conventional magnetocaloric materials until recently. A directed search strategy in the vast space revealed FeMnNiGe_xSi_{1-x} HEAs with magnetocaloric responses that provide the functionality of HEAs comparable to some traditional high-performance magnetocaloric materials (Law *et al.*, 2021a,b), shedding light on applying the HEA design concept for magnetocaloric materials with combined optimal magnetocaloric and mechanical properties.

Due to the hardness and brittleness of magnetocaloric materials, their processing can be challenging using conventional metal manufacturing methods, which is exacerbated by the need to consider a high surface-to-volume ratio in order to transfer heat effectively. Contrary to traditional manufacturing methods, which are primarily based on material removal, additive manufacturing (AM) offers an alternative fabrication approach that involves layer-by-layer deposition of material. This implies practical advantages, including the ease of creating parts that have virtually no shape restrictions and cost savings. Today, the multitude of AM techniques cover the use of almost any type of material, which makes AM a feasible alternative to traditional methods in many technological and industrial areas, including the manufacturing of final functional parts (Fagundes *et al.*, 2022; Zhang *et al.*, 2019). For magnetocaloric technologies, powder bed or powder feed methods are AM techniques that directly print from raw metallic powder using laser, electron-beam, or electric arc sources to melt the material (Frazier, 2014). These techniques have recently been applied to relevant first-order magnetocaloric materials, such as Heusler alloys (Laitinen *et al.*, 2019; Nilsén *et al.*, 2019; Scheibel *et al.*, 2022), La(Fe,Si)₁₃ (Merazzo *et al.*, 2021; Moore *et al.*, 2013) or (Mn,Fe)₂(P,Si) (Christiaanse and Brück, 2014; Miao *et al.*, 2020). However, a reduced magnetocaloric response due to compositional or phase changes caused by the emergence of melting during the additive manufacturing process is commonly found in these cases. This prompts careful optimization of the AM process to account for compositional changes (especially for Mn-based materials) and/or to include a post-processing annealing step to recover the desired magnetocaloric phase. Alternatively, there are other AM techniques that allow the 3D printing of functional parts by means of composites made up of functional fillers embedded in a binder matrix, which will require much lower processing temperatures compared to the previously mentioned methods. In this way, the magnetocaloric fillers do not have to melt, retaining the desired phase for large magnetocaloric performance. In addition, the lower cost of the equipment adds to the interest in these procedures for 3D printing of magnetocaloric parts. Recently used binder materials are inks for inkjet or screen printing (Al-Milaji *et al.*, 2020; Rodríguez-Crespo *et al.*, 2022) and polymers for extrusion-based additive manufacturing (Díaz-García *et al.*, 2022; Sharma *et al.*, 2022). While the non-magnetic binder material can be removed to maximize the response per total mass, in some cases, it can help to preserve the integrity of the built parts, which can deteriorate rapidly under repeated occurrences of the first-order phase transition with significant associated volume changes.

As emphasized throughout the whole article, thermal hysteresis is the primary constraint for first-order magnetocaloric materials, thus a deeper understanding of hysteresis processes is crucial. Regarding this, a recent technique known as TFORC (Temperature First Order Reversal Curves) (Franco *et al.*, 2016) has been developed for studying thermal hysteresis in additional detail. It is based on the analysis of the minor $M(T)$ loops in the hysteretic region of the thermomagnetic transition, the temperature counterpart of the well-known magnetic FORC technique. TFORC technique is in its early development stage, yet it has already been shown that TFORC distributions reflect detailed information about the transformation processes (Díaz-García *et al.*, 2021b; Komlev *et al.*, 2021; Varga *et al.*, 2022). By developing models of the possible transformations, their characteristics are connected to different features of the TFORC distributions, which have been collected in a catalog of differently shaped distributions (analogous to the wishbones and boomerangs found in conventional FORC). This catalog provides useful information about the microscopic details of the transformation (Moreno-Ramírez and Franco, 2020).

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Magnetoelectric Multiferroic Materials

Xiaoshan Xu and Christian Binek, Department of Physics and Astronomy and Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE, United States

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Abstract

Magnetoelectric multiferroics exhibit simultaneous ferroelectric and magnetic orders, which allows a built-in coupling between the two orders, resulting in magnetoelectric effects. Multiferroics are perfect systems for exploring how spin, charge, and lattice, which are often considered independent degrees of freedom in a material, couple to each other. In addition, the potential application of the magnetoelectric effect, especially the electric-field control of magnetism, drives the field toward realizing high-energy-efficiency and scalable memory and logic operations for next generation computing devices. This chapter reviews the key fundamental understanding gained in the past decades of investigation in magnetoelectric multiferroics and the representative material systems.

Nomenclature

$\vec{E}$	electric field
$\vec{P}$	electric polarization
$\vec{H}$	magnetic field
$\vec{M}$	magnetic polarization
$\vec{D}_{AB}$	DM interaction
J	exchange interaction coefficient
$\vec{S}$	spin angular momentum
G	Gibbs free energy
α_{ij}	magnetoelectric susceptibility

Introduction

Multiferroics are materials with multiple ferroic orders (Spaldin *et al.*, 2010; Fiebig *et al.*, 2016; Spaldin, 2017b). Most of the research efforts have been devoted into magnetoelectric multiferroics (Hill, 2000; Ederer and Spaldin, 2004; Hong *et al.*, 2006; Tokura, 2006; Cheong and Mostovoy, 2007; Martin *et al.*, 2008; Khomskii, 2009; Tokura and Seki, 2010; Dong *et al.*, 2019; Lu *et al.*, 2019; Nordlander *et al.*, 2019), which simultaneously exhibit ferroelectricity and magnetism and coupling between the two orders. Ferroelectric materials and ferromagnetic materials have proven to offer a large range of applications such as energy storage and conversion, information storage and processing, sensors, and actuators. Multiferroic materials are expected to inherit the ferroic properties and their applications, making them multifunctional.

More importantly, the coupling between the electric and the magnetic degrees of freedom, called magnetoelectric coupling which generates the magnetoelectric effect, enables novel physical properties and applications. Magnetoelectric effects are possible in materials with broken time-reversal and spatial-inversion symmetry, as indicated in Fig. 1. Of particular interest is electric-field control of magnetism with applications in high-energy-efficiency and scalable memory and logic operations, promising to become a working principle supporting the next-generation computing devices.

Exploration of multiferroics and magnetoelectrics in single-phase materials reveals rich interplay between charge, spin, and lattice, although materials with multiple high ordering temperatures and strong magnetoelectric couplings are yet to be discovered (Dong *et al.*, 2019; Lu *et al.*, 2019; Lottermoser and Meier, 2021). On the other hand, based on the understanding gained from the single-phase materials, composite materials and heterostructures can serve as alternatives with sometimes better functional properties and promising application potentials (Wang *et al.*, 2014; Shevlin, 2019).

This chapter is organized as the follows. In Section “Fundamentals”, we will introduce the fundamental principles behind the multiferroics and magnetoelectric couplings. In Section “Multiferroic Materials”, we go through more details in the representative multiferroic materials. In Section “Magnetoelectric Effects”, magnetoelectric effects and couplings are reviewed.

Fundamentals

By definition, multiferroic materials exhibit magnetic and ferroelectric orders. While the magnetic order breaks the time-reversal symmetry, the ferroelectric order breaks the spatial-inversion symmetry. In addition, broken inversion symmetry due to the magnetic-order may lead to relatively small spontaneous polarization but sizable magnetoelectric coupling. Unravelling the complex magnetic orders and the spin-structure coupling is critical for understanding the plethora of emerging phenomena in multiferroics. In this section, we discuss the fundamental mechanisms such as exchange interaction, magnetic order, spin-induced structure distortion, and the origins of ferroelectricity.

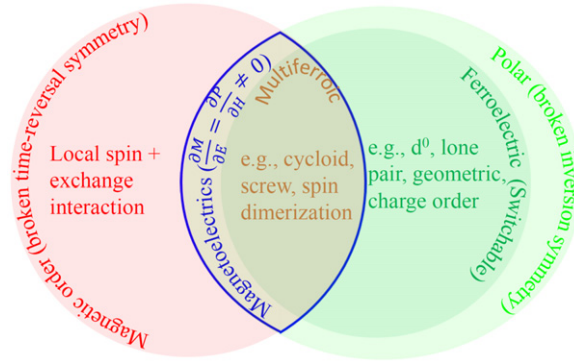


Fig. 1 Venn diagram indicating the relationship between magnetic order, ferroelectricity, multiferroicity, and magnetoelectrics.

Magnetic Interactions

Super-exchange interaction

Magnetic orders of insulators require local spins (magnetic moments). Typically, transition metals with partially filled *d* or *f* orbital states exhibit local magnetic moments. These local moments interact via exchange interactions,

$$J_{AB} \vec{S}_A \cdot \vec{S}_B,$$

where $\vec{S}_A$ and $\vec{S}_B$ are the spins on the interacting sites A and B, and J_{AB} is the exchange interaction energy.

Super-exchange, as a second order process, has been pointed out by [Anderson \(1959\)](#), in insulating compounds where magnetic ions are connected by diamagnetic ligand ions such as O^{2-} and F^- . For example, due to the hybridization between the electron states on the magnetic ions (M_A and M_B) and the ligand O^{2-} , there is finite hopping probability between the hybridized states on M_A and M_B respectively. The hopping allows the exchange through an intermediate state where the two electrons originally on M_A and M_B occupy the same M site. This process can be viewed as hopping of an electron from the ligand to M_A followed by the hopping from M_B to the ligand, as illustrated in [Fig. 2\(a\)](#). Assuming that the hopping energy is t and electron repulsion on the same site is U , the energy correction generated by this process is $J_{AB} = \frac{4t^2}{U}$. It is clear that this process requires that the two electrons on M_A and M_B to have opposite spins, thus favoring the antiferromagnetic spin-spin interactions.

Direct exchange is mediated by the coulomb interaction between the electrons on the two magnetic ions. It favors ferromagnetic spin-spin interactions, but is typically smaller than the super-exchange because of the large separation between the magnetic ions ([Anderson, 1959](#)). On the other hand, it may become more important when the M-ligand-M bond angle is reduced and the super-exchange is weakened.

Dzyaloshinskii–Moriya interaction (DM interaction)

During the study of “weak” ferromagnetism in Fe_2O_3 , [Dzyaloshinsky \(1958\)](#) introduced an interaction that can be written as

$$\vec{D}_{AB} \cdot (\vec{S}_A \times \vec{S}_B).$$

This interaction was later shown by [Moriya \(1960\)](#) to be the antisymmetric version of the exchange interaction when the spin-orbit coupling is considered. Several rules were summarized about the DM interaction according to the symmetry of the interacting magnetic ions. (1) For two magnetic ions A and B, when the point “X” that bisects the line $\vec{r}_{AB}$ that connects the two ion is an inversion center, the DM interaction vanishes. (2) When there is a mirror plane m_v perpendicular to $\vec{r}_{AB}$ passing “X”, $\vec{D}_{AB} \parallel m_v$. (3) When there is a mirror plane m_h including A and B, $\vec{D}_{AB} \perp m_v$. (4) When a two-fold rotation axis C_2 perpendicular to $\vec{r}_{AB}$, $\vec{D}_{AB} \perp C_2$. (5) When there is a n-fold rotation axis passing A and B, $\vec{D}_{AB} \parallel \vec{r}_{AB}$.

As illustrated in [Fig. 2\(b\)](#), consider that the exchange interaction between the two ions are mediated by a third ligand ion, the configuration satisfies the condition (2), (3), and (4). Hence, $\vec{D}_{AB} \parallel m_v$. This is the case in oxide materials where the oxygen local environments of magnetic ions are corner-sharing a polyhedron, such as those in (distorted) perovskite structures. A simple relation $\vec{D}_{AB} \propto \vec{r}_A \times \vec{r}_B$ provides a means to predict the effect of bond angle on the DM interaction ([Keffer, 1962](#); [Cheong and Mostovoy, 2007](#)), which is critical for understanding the cycloid-spin-order induced ferroelectricity (Sections “Inverse Dzyaloshinskii–Moriya interaction” and “Magnetic-induced mechanisms”).

When the magnetic ions are connected by edge-sharing or face-sharing oxygen polyhedra, the exchange interactions are mediated by multiple oxygen ions. For example, for the spin-spin interactions along the *c* axis in the corundum magnetic materials such as Fe_2O_3 , the symmetry for the DM interaction of two magnetic ions has a C_3 rotation axis, which is the orientation of $\vec{D}_{AB}$ ([Dzyaloshinsky, 1958](#); [Moriya, 1960](#); [Dong et al., 2019](#)).

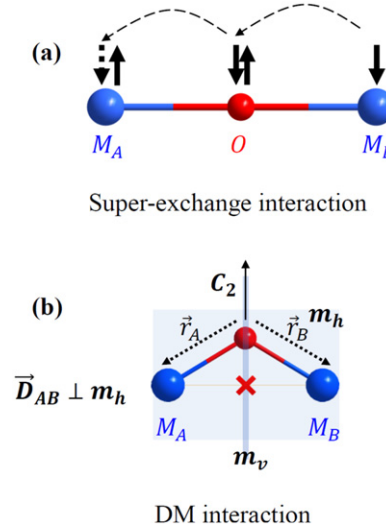


Fig. 2 Illustration of (a) super-exchange and (b) Dzyaloshinskii–Moriya (DM) interaction.

Magnetic Orders (Spin Structures)

The original definition of multiferroics requires ferromagnetic order, *i.e.*, spontaneous magnetization. In practice, it is relaxed to include antiferromagnetic, ferrimagnetic (antiferromagnetic with imbalanced moments), and weak ferromagnetic orders because ferromagnetic insulating materials are rare (Heikes, 1955), especially above room temperature. The plethora of antiferromagnetic orders leads to the complexity and emerging properties of multiferroics. Besides the exchange interaction, geometric arrangement determined by the crystal structures is also an important factor for the formation of magnetic orders or spin structure.

Collinear magnetic structure

Here we use a simple cubic structure arrangement of magnetic sites found in ABO_3 (distorted) perovskite material, where the pseudo cubic coordinates are used.

In the simple cubic structure, when the nearest neighbor exchange interaction is antiferromagnetic and the next nearest neighbor effect is unimportant, G type antiferromagnetic order is formed, as shown in Fig. 3(a). In the G-type antiferromagnets, every spin is surrounded by spins with opposite orientation, which is the case in BiFeO_3 (Kiselev *et al.*, 1963).

With lattice distortion, the degeneracy of the orbital states is lifted, which may cause orbital order and change the spin structure. This has been observed in manganites with Mn^{3+} magnetic ions. When the unit cell is compressed along the z direction (*e.g.*, in orthorhombic RMnO_3 where R is rare earth whose atomic size is larger than Gd (Wollan and Koehler, 1955; Kajimoto *et al.*, 1999; Muñoz *et al.*, 2000; Muñoz *et al.*, 2001; Goto *et al.*, 2004; Hemberger *et al.*, 2007; O’Flynn *et al.*, 2011)), causing the local environment MO_6 to squeeze toward an oblate shape, the degeneracy of the e_g states is lifted: the $x^2 - y^2$ state has lower energy than that of the z^2 state. For the $3d^4$ configuration in Mn^{3+} , the $x^2 - y^2$ state is occupied while the z^2 state is empty. This leads to the A type spin structure where within the x - y plane, the spins are ferromagnetically aligned, while they are antiferromagnetically aligned along the z direction, as shown in Fig. 3(b).

If the unit cell is elongated along the z direction (*e.g.*, in $\text{Nd}_{0.25}\text{Mn}_{0.75}\text{O}_3$) (Kajimoto *et al.*, 1999), the z^2 state is occupied because it has lower energy, which leads to the C type spin structure where the spins are antiferromagnetically aligned within the x - y plane, but ferromagnetically aligned along the z direction, as shown in Fig. 3(c).

Non-collinear magnetic structure

When the next nearest neighbor exchange interaction is antiferromagnetic and large enough, modulations of spin orientations, which often generate non-collinear or spiral spin structures, are expected. This can be understood using a simple 1D model of exchange energy (Majlis, 2000)

$$E = -J_1 \sum_n \vec{S}_n \cdot \vec{S}_{n+1} - J_2 \sum_n \vec{S}_n \cdot \vec{S}_{n+2},$$

where J_1 and J_2 are the nearest-neighbor and the next-nearest-neighbor exchange coefficients, $\vec{S}_n$ are the spin at the n^{th} site. The stable spin structures are the following: (1) If $\frac{J_2}{J_1} < -\frac{1}{4}$, the modulation $\vec{S}_n = \vec{S}_k e^{ikR_n}$ is stable with $\cos(ka) = -\frac{J_1}{4J_2}$, where $R_n = na$ is the position of the n^{th} site. This means that the next-nearest-neighbor exchange interaction needs to be antiferromagnetic in nature and its magnitude needs to be large enough ($|\frac{J_2}{J_1}| > \frac{1}{4}$). (2) If $J_1 > 0$ and $\frac{J_2}{J_1} > -\frac{1}{4}$, a collinear ferromagnetism structure is stable. (3) If $J_1 < 0$ and $\frac{J_2}{J_1} > -\frac{1}{4}$, a collinear antiferromagnetic structure is stable.

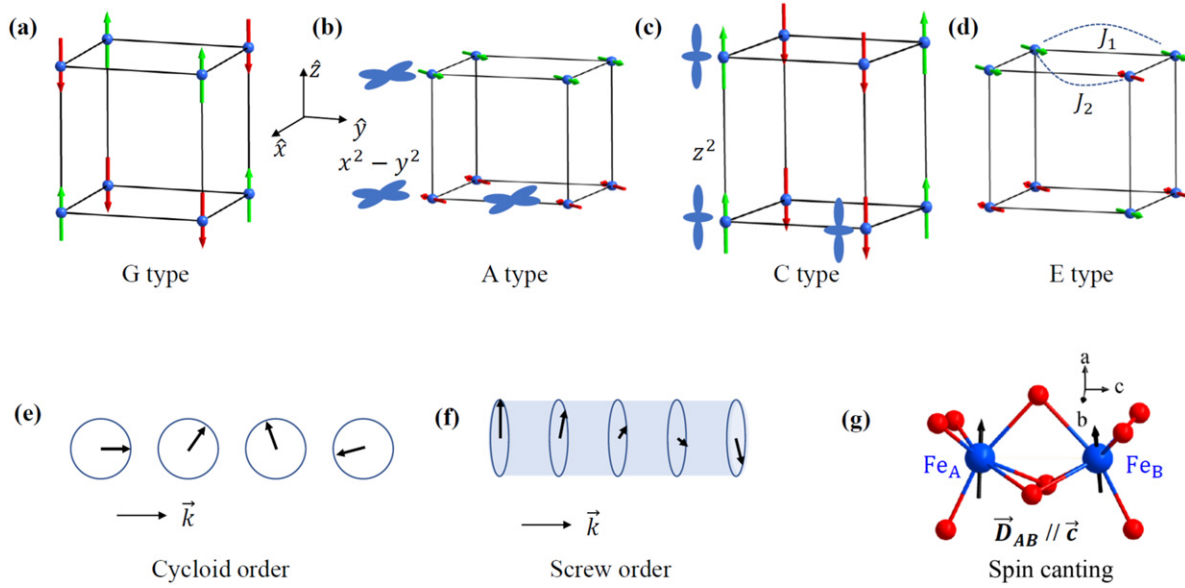


Fig. 3 Spin structures. (a)–(d) are collinear G type, A type, C type, and E type in simple cubic arrangement of magnetic sites. (e) and (f) are non-collinear cycloid and screw spin structures. (g) is the local spin canting due to the DM interaction.

In orthorhombic RMnO_3 where R is rare earth whose atomic size is smaller than Dy (such as Ho and Lu) (Muñoz *et al.*, 2001; Goto *et al.*, 2004; Okamoto *et al.*, 2008; Chai *et al.*, 2012), on top of the A-type spin structure, a modulation is developed with the propagation vector $\vec{k} = (\frac{1}{4}, \frac{1}{4}, 0)$, which forms the E-type spin structure, as shown in Fig. 3(d) near here.

When the modulation is incommensurate and the propagation vector $\vec{k}$ is in the plane of varying spins, a cycloid order is formed, as observed in TbMnO_3 and DyMnO_3 and illustrated in Fig. 3(e) near here (Kimura *et al.*, 2003, 2005; Goto *et al.*, 2004; Kajimoto *et al.*, 2004; Aoyama *et al.*, 2014). On the other hand, if the propagation vector $\vec{k}$ is perpendicular to the plane of varying spins, a screw order is formed, which is illustrated in Fig. 3(f) near here and is observed in Cu(FeAl)O_2 (Arima, 2007; Nakajima *et al.*, 2009).

Spin canting

The DM interaction can also cause deviation from the collinear magnetic structure by canting the spins. As shown in Fig. 3(g), in Fe_2O_3 , between the two neighboring Fe^{3+} (A and B) along the c axis, the C_3 rotational symmetry along the c axis forces $\vec{D}_{AB} \parallel \vec{c}$. (Moriya, 1960) When the two spins are perpendicular to the c axis, a non-collinear arrangement is favored due to the non-zero $\vec{S}_A \times \vec{S}_B$ that can minimize the DM-interaction energy, corresponding to the spin canting. Spin-canting is commonly observed in materials (Dzyaloshinsky, 1958; Munoz *et al.*, 2000; Guidi *et al.*, 2001; Wang *et al.*, 2013) since all it requires is the loss of local inversion symmetry and spin not lying along the $\vec{D}_{AB}$ direction.

Spin-induced Lattice Distortions

The coupling of local spin structure to the crystal structure is the key for magnetoelectric coupling and the spin-induced ferroelectric orders.

Spin-dependent hybridization

Spin-dependent hybridization is directly related to the interplay between the orbital and spin states based on the spin-orbit coupling. Due to the spin-orbit interaction, the spin states develop a preference of orientation, often manifested as single-ion magnetic anisotropy. The inverse effect is when the spin is forced toward a different direction, *e.g.*, due to the external field or the exchange interaction, the orbital state will change, which often manifests in magnetoelastic effects (O'Handley, 2000).

Fig. 4(a) illustrates an example using a two-ion model where an O^{2-} ion and a 3d transition metal ion are connected. Here the z axis is along the line connecting the two ions and the π bonding between the $l_z = \pm 1$ states of the oxygen and the M ions is considered, where l_z is the projection of angular momentum along the z axis. Spin-orbit coupling split the $l_z = \pm 1$ states on the oxygen ion ($p_{\pm 1}$) and that on the M ion ($d_{\pm 1}$) by $\lambda_p S_z$ and $\lambda_d S_z$ respectively, where λ_p and λ_d are the spin-orbit coupling strength on the p state of the O and the d state of the M ions respectively, S_z is the projection of spin on the z direction. If only the lower bonding state is concerned, due to the spin-orbit coupling, the modified energy difference between the p and the d states is

$$\Delta E = \Delta_{pd} - (\lambda_p - \lambda_d) S_z^2,$$

where Δ_{pd} is the value without the spin-orbit coupling. This in turn changes the hybridization (mixing between the two states) and causes a local dipole proportional to S_z^2 (Arima, 2007).

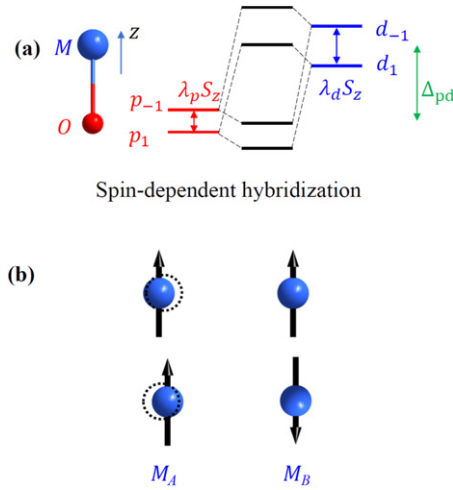


Fig. 4 Spin-induced local distortions. (a) Spin-dependent hybridization. (b) Exchange striction.

This effect can be extended to multiple M sites (Jia *et al.*, 2006). For example, in a M_A -O- M_B linear structure, it was shown that the competition between the spin-dependent hybridization on two sides of the O ligand results in a local dipole proportional to $S_{z,A}^2 - S_{z,B}^2$, where $S_{z,A}$ and $S_{z,B}$ are the projection of spins along the z direction on the A and B sites respectively.

Exchange striction

The inverse effect of exchange interaction can also affect the local structure. The exchange interaction coefficient J_{AB} relies on the electronic states which are determined by the local structure. As the inverse effect, the spin alignment is expected to modify the local structure. As illustrated in Fig. 4(b), since the exchange interaction $J_{AB} \vec{S}_A \cdot \vec{S}_B$ contributes to the bonding energy, when the spin alignment changes, the total energy changes, which causes the relaxation of the local structure to minimize the total energy, leading to the exchange striction (Choi *et al.*, 2008). A key difference between exchange striction and the spin-dependent hybridization is that the former is proportional to $\vec{S}_A \cdot \vec{S}_B$ which is isotropic, while the latter depends on the angular momentum of orbital states which is anisotropic.

Inverse Dzyaloshinskii–Moriya interaction

As illustrated in Fig. 2(b), in the DM interaction $\vec{D}_{AB} \cdot \vec{S}_A \times \vec{S}_B$, $\vec{D}_{AB}$ is determined by the local structure. Given a certain spin alignment, a distortion of structure may modify $\vec{D}_{AB}$ and the DM interaction energy, which causes the instability of local structures.

Origin of Ferroelectricity

Ferroelectric materials all exhibit spontaneous polarization that is switchable by an external field, which requires the broken spatial inversion symmetry. In most ferroelectrics, the broken inversion symmetry can be clearly seen from the crystal structure, corresponding to the non-magnetism mechanism. Novel, magnetic-induced mechanisms discovered in multiferroics, suggest that the spin structure that breaks the inversion symmetry also allows the development of spontaneous polarization, although with a much smaller magnitude.

Non-magnetic mechanisms

When the ferroelectric order results directly from the reduction of free energy due to the spontaneous polarization, the ferroelectricity is called proper.

A prototype of proper ferroelectric is PbTiO_3 . The $3d^0$ state of the Ti^{4+} ions allows it to displace toward one of the O^{2-} ions in the TiO_6 octahedra for hybridization to minimize the energy (Cohen, 1992) in response to the atomic size mismatch between Ti^{4+} and Pb^{2+} , as shown in Fig. 5(a). This mechanism is often referred to as the d^0 -ferroelectricity (Hill, 2000).

Another mechanism of proper ferroelectricity, called lone-pair ferroelectricity (Seshadri and Hill, 2001), is observed in BiFeO_3 . In Bi^{3+} , the $6s^2$ electrons, or the lone-pair, occupy the corner of the cubic local environment due to the repulsion from the negative O^{2-} ions (similar to how a water molecule gains the dipole moment). This causes a displacement of Bi^{3+} along the (111) direction in the pseudo cubic coordinates and the corresponding polarization, as shown in Fig. 5(b).

For improper ferroelectricity, the spontaneous polarization is induced by a non-polar structure distortion that breaks the inversion symmetry. As shown in Fig. 5(c), in hexagonal RMnO_3 or RFeO_3 ($R=\text{Ho-Lu, Y, Sc}$) (Van Aken *et al.*, 2001), the mismatch between the cation sizes causes the so-called K_3 distortion which can be described as the rotation of the trigonal bipyramids and the buckling of the R layer (Fennie and Rabe, 2005). Due to the hexagonal symmetry, the K_3 distortion, although

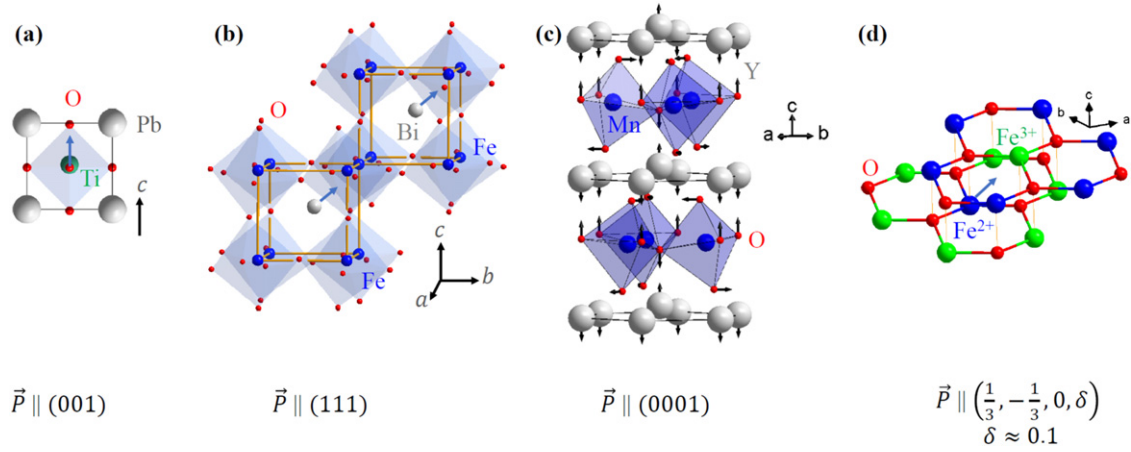


Fig. 5 Non-magnetic mechanisms of ferroelectricity. (a) The d^0 mechanism in which the ion in the center needs a d^0 configuration to displace away from the center and hybridize with O ions. (b) The lone-pair mechanism in which the displacement comes from the Coulomb repulsion between the lone pair and O ions. (c) The geometric frustration mechanism in which the lattice distortion (represented using the atomic displacements indicated by the arrows) in the unit cell of hexagonal symmetry breaks the inversion symmetry. (d) The charge order mechanism in which the order of charge (or valence) of ions generates local dipole.

non-polar by itself, breaks the inversion symmetry and induces the uneven displacements of atoms along the c axis, or the Γ_2^- distortion that brings the spontaneous polarization (Fennie and Rabe, 2005). This mechanism is also called geometric ferroelectricity due to the critical role of the hexagonal geometry.

Another possible improper mechanism for ferroelectricity, from charge order, has been proposed in LuFe_2O_4 (Ikeda *et al.*, 2005). As shown in Fig. 5(d), in the two neighboring FeO layers, the population of Fe^{3+} and Fe^{2+} are ordered with one layer dominated by Fe^{3+} and the other dominated by Fe^{2+} , which leads to a dipole between the two layers, along the $\left(\frac{1}{3}, -\frac{1}{3}, 0, \delta\right)$ direction where $\delta \approx 0.1$, in the hexagonal coordinates. On the other hand, although the charge order is confirmed, whether that leads to ferroelectricity in LuFe_2O_4 is under debated (Angst *et al.*, 2008; Xu *et al.*, 2010). Nevertheless, the superlattice of hexagonal LuFeO_3 and LuFe_2O_4 leads to enhanced multiferroic properties (Mundy *et al.*, 2016).

Magnetic-induced mechanisms

Given the mechanisms on the spin-induced lattice distortions in the Section "Spin-induced Lattice Distortions" Exchange striction with the appropriate spin order, spontaneous polarization and ferroelectric order can be generated.

The spin-current mechanism (Katsura *et al.*, 2005) relies on the cycloid spin order. As shown in Fig. 6(a), in TbMnO_3 , a spin cycloid order is formed with a propagation vector $\vec{Q} \parallel (0, 1, 0)$ in the orthorhombic Pbnm coordinates (see Section "Non-collinear magnetic structure") (Kimura *et al.*, 2003, 2005; Goto *et al.*, 2004; Kajimoto *et al.*, 2004; Aoyama *et al.*, 2014). This spin order breaks the inversion symmetry, allowing a spontaneous polarization along c axis. The symmetry of the effect can be summarized using $\vec{P} \propto \vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j)$, where $\vec{e}_{ij}$ is the vector connecting the two magnetic sites with spin $\vec{S}_i$ and $\vec{S}_j$. Microscopically, the non-zero $\vec{S}_A \times \vec{S}_B$ between neighboring sites due to the cycloid order leads to a finite DM interaction energy. As illustrated in Fig. 6(a), along the M-O-M chain, the ligand O^{2-} displaces to minimize the DM interaction energy. In TbMnO_3 , the displacements results in a collective spontaneous polarization along the c axis (Kimura *et al.*, 2003).

The spin-dependence-hybridization mechanism can generate spontaneous polarization with a screw spin order. As shown in Fig. 6(b), in $\text{Cu}(\text{FeAl})\text{O}_2$ (Arima, 2007; Nakajima *et al.*, 2009), the propagation vector in the basal plane is $\vec{Q}_{\text{in}} \parallel (1, 1)$ in the hexagonal coordinates. This spin order breaks the inversion symmetry, allowing a spontaneous polarization along screw axis $\vec{Q}$. Microscopically, due to the modulation of spin orientations, the length of the chemical bonds connecting an M site and a ligand O^{2-} site, which depends on the hybridization of the M and ligand states, is also modulated. The net polarization is only possible when the modulation is incommensurate given the symmetric crystal structure.

In the exchange-striction mechanism, a dimerization of different species of magnetic ions is the key. As shown in Fig. 6(c), in $\text{Ca}_3\text{CoMnO}_6$, magnetic Co^{2+} and Mn^{4+} ions are lined up with a collinear $\uparrow\uparrow\downarrow$ spin structure pattern along the c axis (Choi *et al.*, 2008; Wu *et al.*, 2009; Zhang, Xiang and Whangbo, 2009). The total exchange energy can be written as

$$E = - \left(J_0 + \frac{\partial J}{\partial z} \delta \right) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Co}} + \left(J_0 + \frac{\partial J}{\partial z} \delta \right) \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Co}} = - 2 \frac{\partial J}{\partial z} \delta \vec{S}_{\text{Mn}} \cdot \vec{S}_{\text{Co}},$$

where $\vec{S}_{\text{Mn}}$ and $\vec{S}_{\text{Co}}$ are spins on Mn and Co ions, J_0 is the exchange interaction coefficient without dimerization, and δ is the atomic displacement of the dimerization. It is clear that the dimerization (non-zero δ) lowers the energy. The dimerization in the spin structure breaks the inversion symmetry and in turn generates a net polarization because of the charge difference between Co^{2+} and Mn^{4+} .

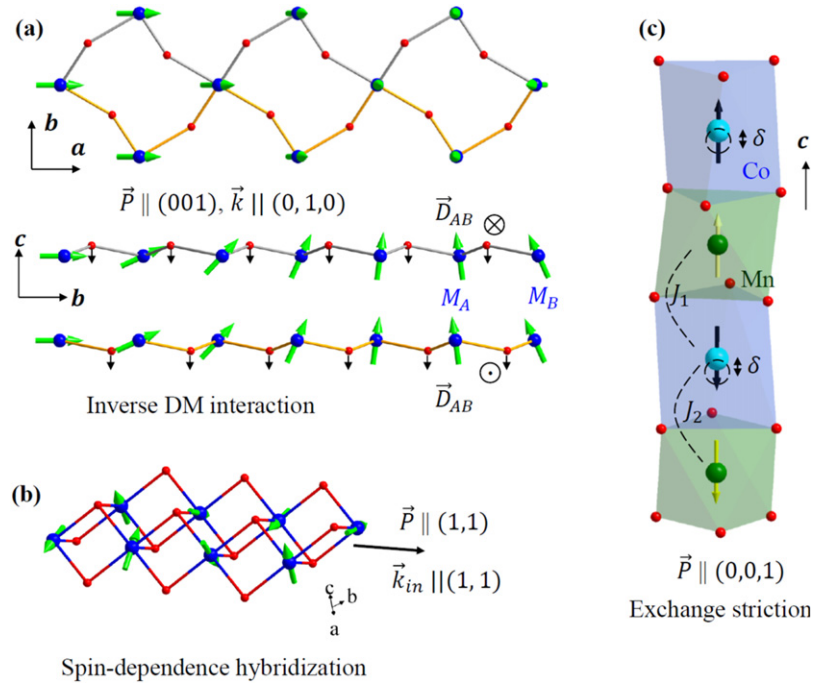


Fig. 6 Magnetic-induced mechanisms of ferroelectricity. (a) Inverse DM interaction mechanism based on spin cycloid which breaks the inversion symmetry in TbMnO_3 . Thin arrows indicate atomic displacements. (b) Spin-dependent hybridization mechanism based on incommensurate spin screw which breaks the inversion symmetry in CuFeO_2 . (c) Exchange striction mechanism based on up-up-down-down spin structure which leads to dimerization in $\text{Ca}_3\text{CoMnO}_6$. J_1 and J_2 are exchange interaction coefficients. δ is the atomic displacements.

Multiferroic Materials

Multiferroics with ferromagnetism and ferroelectricity of large ($> 1 \mu\text{C}/\text{cm}^2$) polarizations are extremely rare, especially above room temperature (Hill, 2000). On the other hand, there is a sizable number of multiferroics when the condition is relaxed to include antiferromagnetic order, weak ferromagnetism, and ferroelectricity with small polarizations. Khomskii (2009) classified multiferroics into type I in which magnetic and ferroelectric orders are of distinct origins, and the type II whose ferroelectricity originate from magnetic orders that break inversion symmetry.

Type I

The ferroelectric and the magnetic order of Type I multiferroics comes from distinct origins. This allows high ordering temperatures and large polarizations. Although strong magnetoelectric coupling is not expected, the interplay between the electric and magnetic degrees of freedoms does manifest in subtle details.

EuTiO_3

In the intensively studied ABO_3 perovskite material family, ferroelectricity may occur when the B site has the d^0 electronic configuration, e.g., in PbTiO_3 (see Section “Non-magnetic mechanisms”). When the B site has partially filled d states, magnetic ordering develops. Thus the requirements for ferroelectric and magnetic orders for the B site is incompatible (Hill, 2000). On the other hand, in EuTiO_3 , the magnetic order is obtained via the magnetic ions on the A site (Eu^{2+}) (Lee et al., 2010).

Bulk EuTiO_3 has a cubic Pm-3m structure with inversion symmetry, which precludes ferroelectricity. Below $T_N \approx 5.4\text{K}$, the magnetic Eu^{2+} ions in EuTiO_3 form a G-type antiferromagnetic order (Lee et al., 2010). Interestingly, under the biaxial tensile strain, EuTiO_3 becomes ferroelectric. When EuTiO_3 thin films are epitaxially grown on $\text{DyScO}_3 (110)_o$ plane, corresponding to the $(001)_{pc}$ plane in pseudo cubic coordinates, an approximately 1.1% biaxial tensile strain is applied. As illustrated in Fig. 7(a), the tensile strain induces a displacement of Ti^{4+} along the $(1-10)_{pc}$ direction and the corresponding spontaneous polarization below $T_C \approx 250\text{K}$ (Lee et al., 2010; Ke et al., 2013).

First principles calculations indicate the importance of the third nearest neighbor exchange interactions between Eu^{2+} ions along the $(111)_{pc}$ direction (Ke et al., 2013; Ryan et al., 2013; Zhao et al., 2022). Moreover, this exchange interaction is mediate by the Ti^{4+} in the center of the unit cell, which makes it sensitive to the Ti^{4+} displacements. With the $(1-10)_{pc}$ displacement of Ti^{4+} (Ke et al., 2013), the third nearest exchange interaction turns from antiferromagnetic to ferromagnetic, which leads to the ferromagnetic order below $T_C \approx 4.3\text{K}$.

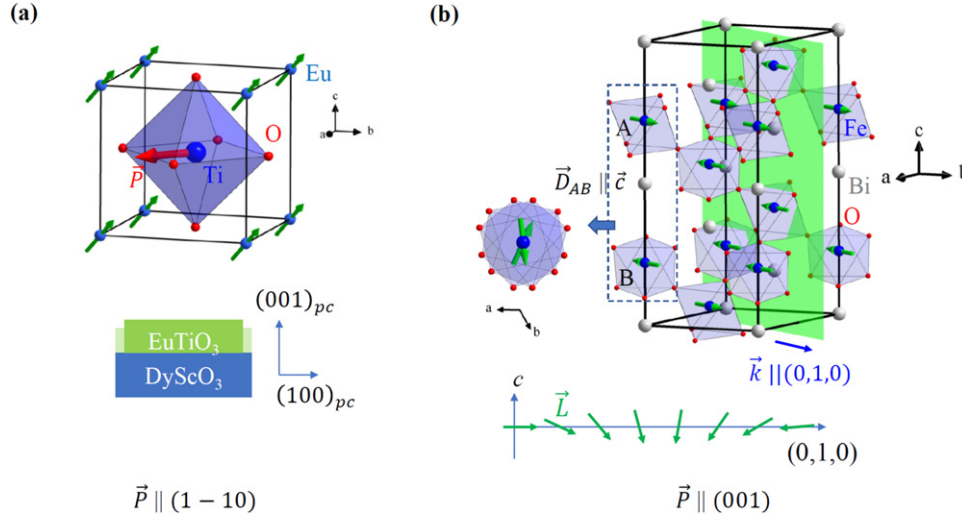


Fig. 7 (a) Crystal and spin structure of EuTiO₃ in thin films of tensile biaxial strain. (b) BiFeO₃ in hexagonal coordinates showing the crystal structure, spin structure, and the spin canting due to the DM interaction.

Coupling between the ferroelectric and magnetic order manifest first in the single-ion magnetic anisotropy, which is predicted to be along the $(111)_{pc}$ direction that is perpendicular to the polarization (Ke *et al.*, 2013). More importantly, since the exchange interaction hinges on the polarization, the magnetic order can be switched between the ferromagnetic and antiferromagnetic using an electric field that controls the induced polarization (Ryan *et al.*, 2013).

BiFeO₃

The coexistence of ferroelectric and magnetic orders can also be realized utilizing the A-site displacements, which is the case in BiFeO₃, arguably the most studied multiferroic materials to date (Wang *et al.*, 2003; Zhao *et al.*, 2006; Chu *et al.*, 2008; Heron *et al.*, 2014), due to the high ferroelectric ($T_C = 1100\text{K}$) ordering temperature (Kiselev *et al.*, 1963), large ($50\text{--}100 \mu\text{C}/\text{cm}^2$) electric polarizations (Wang *et al.*, 2003; Lebeugle *et al.*, 2007), and high transition temperature ($T_N = 640\text{K}$) of the antiferromagnetic order (Kiselev *et al.*, 1963).

The crystal structure of BiFeO₃ belongs to the rhombohedrally distorted ABO₃ perovskite (space group $R3c$), in which the A sites (Bi) displace along the (111) pseudo-cubic direction, corresponding to the lone-pair type ferroelectricity (Seshadri and Hill, 2001) shown in Fig. 5(b).

In the short-range (unit-cell scale), BiFeO₃ features the G-type antiferromagnetic order (Kiselev *et al.*, 1963), as shown in Fig. 7(b) in a hexagonal unit cell. Along the c axis, the DM interaction between the magnetic Fe^{3+} sites are determined by the 3-fold rotational axis ($\vec{D} \parallel \vec{c}$). Therefore, when the Fe^{3+} spins have non-zero projections within the basal plane, the spins deviate from the perfect G type arrangement to form a small in-plane angle and a local canted magnetic moment (Xu *et al.*, 2019).

Coupling between the ferroelectric and magnetic orders in BiFeO₃ manifest in the incommensurate spin cycloid (period $\approx 64 \text{ nm}$) with propagation vector $\vec{Q} \parallel (0, 1, 0)$, which describes the magnetic structure on a larger scale (Sosnowska *et al.*, 1982; Sosnowska *et al.*, 1992; Sosnowska and Zvezdin, 1995; Kadomtseva *et al.*, 2004; Przeniosło *et al.*, 2006). The spin cycloid is a results of interplay between exchange interaction, magnetic anisotropy, and inhomogeneity energy, as describe by the free energy

$$F = -\alpha \vec{P} \cdot [\vec{L} (\nabla \cdot \vec{L}) - (\vec{L} \cdot \nabla) \vec{L}] + \beta (\nabla \cdot \vec{L})^2 - \gamma (\vec{L} \cdot \vec{P})^2$$

where $\vec{P}$ and $\vec{L}$ are the polarization and the antiferromagnetic order parameter respectively, α , β , and γ are the coefficients for the inhomogeneity, exchange interaction, and magnetic anisotropy. While the first term favors spin inhomogeneity, the exchange (second) term keeps the variation small; the anisotropy (third) term ensures $\vec{P}$ is in the cycloid plane. An important consequence of the spin cycloid is that it makes the sum of the canted magnetic moments zero. An exception happens in thin films of BiFeO₃ where the epitaxial strain and truncation of the period of the spin cycloid gives rise to a weak ferromagnetic moment (Bai *et al.*, 2005; Zhao *et al.*, 2006; Haykal *et al.*, 2020).

Hexagonal RMnO₃ and RFeO₃

Hexagonal manganites (h-RMnO₃) and ferrites (h-RFeO₃) $R = \text{Sc, Y, Ho-Lu}$, are isomorphic with the $P6_3cm$ structure (Van Aken *et al.*, 2001; Xu and Wang, 2014), which features a MnO (or FeO) layer and a RO₂ layer in hexagonal stacking. While the hexagonal structure of RMnO₃ is stable, h-RFeO₃ can be stabilized in epitaxial thin films (Xu and Wang, 2014). As shown in Fig. 8(a), the driving force of the ferroelectricity is the non-polar K_3 structure distortion, which breaks the inversion symmetry but does not directly generate polarization (Fennie and Rabe, 2005). On the other hand, the K_3 distortion induces the Γ_2^- structural distortion (Fig. 8(a) near here) with displacements of atoms along the c axis and the corresponding polarization below $T_C \approx 1000\text{K}$ (Van Aken *et al.*,

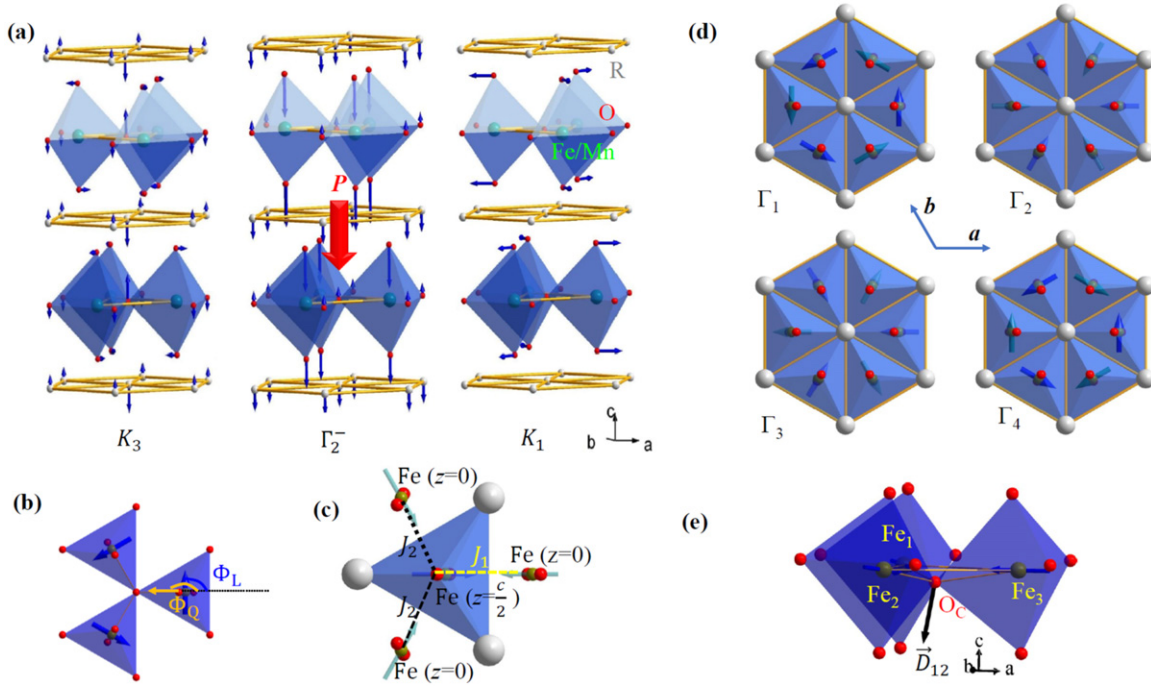


Fig. 8 h-RMnO₃ and h-RFeO₃. (a) Three structural distortions relative to the high-temperature paraelectric state. (b) The definition of the K_3 rotation angle (Φ_Q) and the in-plane spin direction (Φ_L). (c) Geometry of the exchange interaction between Fe sites of neighboring planes ($z = 0$ and $z = c/2$). (d) Four different possible spin structures. (e) Schematics for the Fe spin canting due to the DM interaction.

2001; Xu and Wang, 2014). This origin of improper ferroelectricity can be described using the free energy in the Landau theory (Artyukhin *et al.*, 2014; Yun *et al.*, 2022),

$$F = \frac{a_c}{2} Q^2 + \frac{b_c}{4} Q^4 - g_c Q^3 P \cos 3\Phi_Q + \frac{g'_c}{2} Q^2 P^2 + \frac{a_{pc}}{2} P^2,$$

where Q is the magnitude of the K_3 distortion, P is the polarization, Φ_Q is the direction (phase) of the K_3 distortion (Fig. 8(b) here), a_c , b_c , g_c , g'_c , and a_{pc} are coefficients. The first two terms $\frac{a_c}{2} Q^2 + \frac{b_c}{4} Q^4$ determine the magnitude of the K_3 distortion. The third term describes the coupling between the distortion and the polarization. This term, which is linear with P , is a key feature of the improper ferroelectricity in h-RMnO₃ and h-RFeO₃, which prevents the depolarization energy from quenching the spontaneous polarization and imposing a critical thickness (Sai *et al.*, 2009; Nordlander *et al.*, 2019; Yun *et al.*, 2022)

Both h-RMnO₃ and h-RFeO₃ adopt the 120-degree in-plane spin structures, where the spins are essentially in the basal plane (Munoz *et al.*, 2000; Xu and Wang, 2014). While the in-plane exchange interaction is strong, the effective out-of-plane exchange interaction is weakened by the symmetry (Sinha *et al.*, 2018). As shown in Fig. 8(c), an Mn/Fe site is in the center of the triangle formed by its three nearest neighbors in the adjacent layer; the sum of the spins of these three neighbors is zero. Hence, the inter-layer exchange interaction energy E_{ex} is non-zero only because the K_3 distortion breaks the three-fold rotational symmetry, i.e., $E_{ex} \propto (J_1 - J_2) S^2 \propto Q S^2$, where S is the spin on the Mn/Fe sites. This relation explains two observations about the three dimensional magnetic ordering temperature T_N : (1) T_N is higher in h-RFeO₃ compared with that in h-RMnO₃ because of the larger S of Fe³⁺ compared with that of Mn³⁺ (Fiebig *et al.*, 2003; Jeong *et al.*, 2012; Wang *et al.*, 2013; Disseler *et al.*, 2014, 2015; Moyer *et al.*, 2014; Yokota *et al.*, 2015; Sinha *et al.*, 2018; Yun *et al.*, 2022) (2) T_N is the largest (≈ 130 and 200K in h-RMnO₃ and h-RFeO₃ respectively) for the largest Q which occurs when $R = \text{Sc}$ (Munoz *et al.*, 2000; Sinha *et al.*, 2018).

The in-plane orientation of spins described by the angle $\Phi_L - \Phi_Q$ is different for h-RMnO₃ and h-RFeO₃, which is determined by the single-ion magnetic anisotropy related to the K_1 lattice distortion in Fig. 8(a) (in-phase with the K_3), where Φ_L is orientation of the spin (Cao *et al.*, 2016). Most h-RMnO₃ exhibit the Γ_1 or Γ_4 spin structure, as shown in Fig. 8(d) (Fiebig *et al.*, 2003). In contrast, h-RFeO₃ are found to have the Γ_2 spin structure (Xu and Wang, 2014). The symmetry of the Γ_2 and Γ_3 spin structures allows for the canting of spin out of the basal plane, while only Γ_2 leads to the net magnetization, which is case for h-RFeO₃ with a magnitude of $\sim 0.01 \mu_B/\text{f.u.}$ (Sinha *et al.*, 2018).

The spin canting originates from the DM interaction. As shown in Fig. 8(e), due to the K_3 distortion (downward displacement of the central atom O_c), the DM interaction coefficient $\vec{D}_{12}$ is tilted away from the c axis. To minimize the DM interaction energy, the spins cant out of the basal plane. The competition between the exchange interaction and the DM interaction determines the canting angle as (Sinha *et al.*, 2018)

$$\theta \approx \frac{D_{12}}{\sqrt{3}J} \phi,$$

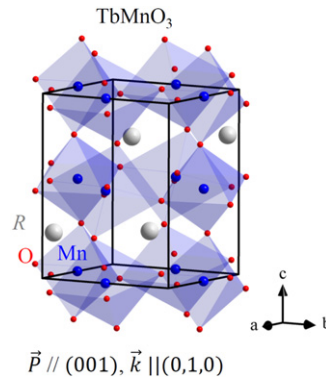


Fig. 9 Orthorhombic $RMnO_3$. Crystal structure of Pbnm space group showing the rotation and tilt of the octahedra.

where ϕ is the tilt angle of $\vec{D}_{12}$, J is the in-plane exchange interaction coefficient. Since typically $D_{12} \ll J$, one has $\theta \ll \phi$, which is consistent with the observation that $\theta \sim 0.1^\circ$ and $\phi \sim 1^\circ$.

Coupling between the ferroelectric and the magnetic order is mediated by the K_3 lattice distortion, which is the key for both the spontaneous polarization, 3D magnetic order, single-ion magnetic anisotropy, and the spin canting, as discussed above. The effects turns out to be the most significant at the ferroelectric domain walls (Artyukhin *et al.*, 2014). Between the two sides of a ferroelectric domain wall, both Φ_Q and Φ_L change by $\frac{\pi}{3}$ (Artyukhin *et al.*, 2014; Das *et al.*, 2014). On the other hand, in contrast to the abrupt change of Φ_Q , Φ_L changes much more gradually, generating a “clamped” magnetic domain wall in which $\Phi_L - \Phi_Q$ does not fully follow the bulk spin structure, which changes the local magnetization. The effect is particularly significant in h- $RMnO_3$, where the clamped magnetic domain walls exhibit finite magnetization in the background of zero-magnetization domains (Fiebig *et al.*, 2002; Ueland *et al.*, 2010; Geng *et al.*, 2012; Artyukhin *et al.*, 2014).

Type II

In Type II multiferroics, ferroelectric orders come from complex magnetic order that breaks the spatial inversion symmetry, which means that the ferroelectric order can be controlled by manipulating the magnetic order using a magnetic field, corresponding to the intrinsic, strong coupling. The material introduced below are selected to exemplify magnetic-field controlled polarization flop (orthorhombic $RMnO_3$) and reversal ($TbMn_2O_5$), and electric-field controlled magnetization reversal (orthorhombic $RFeO_3$).

Orthorhombic $RMnO_3$ ($R = Tb, Dy$)

Similar to many other ABO_3 distorted perovskite materials, when the atomic size of R is larger than that of Ho , $RMnO_3$ adopt an orthorhombic structure described by the Pbnm (62) space group, as shown in Fig. 9.

When $R = Tb$ and Dy , cycloid spin structure occurs in $RMnO_3$ (Goto *et al.*, 2004; Kimura *et al.*, 2005). The phase diagram of $TbMnO_3$ (Kimura *et al.*, 2003, 2005; Goto *et al.*, 2004; Kajimoto *et al.*, 2004) summarizes the complex magnetic structure and the origin of ferroelectricity. Below $T_N \approx 41K$, $TbMnO_3$ becomes antiferromagnetic with an incommensurate sinusoidal order of Mn^{3+} moments with propagation vector along $\vec{k} = (0, k_s, 1)$ in the orthorhombic coordinates, where $k_s \approx 0.295$ which varies with temperature. Below $T_{lock} \approx 27K$, the spin order becomes the cycloid in the b - c plane, with $\vec{k} = (0, k_s, 0)$ and k_s locks at approximately 0.28, triggering a spontaneous polarization along the c axis (see Sections “Non-collinear magnetic structure” and “Magnetic-induced mechanisms”). Below $T_N(Tb) \approx 7K$, the magnetic moment on Tb^{3+} forms the antiferromagnetic order.

Below T_{lock} , when a high enough magnetic field is applied along the b axis, spontaneous polarization “flop” from the c axis to the a axis. This is interpreted as Tb^{3+} moment reversal that causes the reorientation of the Mn^{3+} spin cycloid to the a - b plane and the corresponding electric polarization (Kimura *et al.*, 2003). The magnetic-field-induced polarization flop represent one of the most dramatic magnetoelectric coupling achieved in multiferroics, although the temperature of the effect is below 30K and the effect is volatile.

RMn_2O_5 ($R = \text{rare earth, Y, and Bi}$)

Materials with more complex structures like RMn_2O_5 offer more intricate magnetic structures and more dramatic couplings to the electric degrees of freedom. RMn_2O_5 crystallizes in a orthorhombic structure with the Pbam space group. The Mn^{4+} ions occupy the oxygen octahedra, while the Mn^{3+} ions locate in the oxygen square pyramids (Gardner *et al.*, 1988; Kagomiya *et al.*, 2002).

Below $T_N \approx 43K$, an incommensurate helical spin order is formed with a propagation vector $\vec{k} \approx (0.5, 0, 0.3)$ with the Mn spins lying in the a - b plane, as shown in Fig. 10 near here. The helical structure is a result from the competing exchange interactions. Below about 33K, an commensurate order locks in with $\vec{k} \approx (0.5, 0, 0.25)$, which becomes incommensurate again at lower temperature (Gardner *et al.*, 1988; Chapon *et al.*, 2004; Hur *et al.*, 2004; Kobayashi *et al.*, 2004b).

The frustrated spin structure, especially among the five-Mn rings, leads to the small structural distortion to lower the local symmetry, which is referred to as the magnetic Jahn-Tell effect (Tchernyshyov *et al.*, 2003). This structural distortion causes a small polarization and

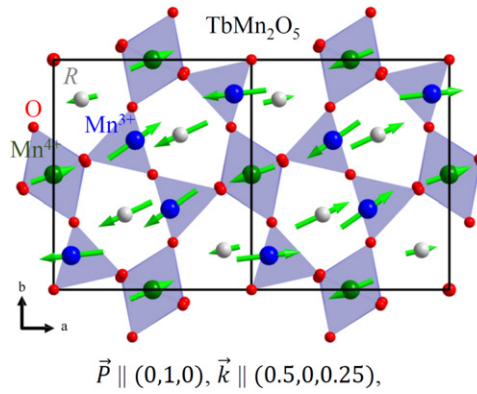


Fig. 10 RMn_2O_5 . Projection of typical spin structure on the a - b plane with propagation vector $\vec{k} \approx (0.5, 0, 0.25)$.

the corresponding ferroelectricity (Inomata and Kohn, 1996; Kagomiya, Kohn and Uchiyama, 2002; Chapon *et al.*, 2004; Hur *et al.*, 2004; Kobayashi *et al.*, 2004a,b). This scenario also fits the spin-current mechanism discussed in Section “Magnetic-induced mechanisms”, because $\vec{k} \times (\vec{S}_i \times \vec{S}_j) \parallel \vec{b}$ is consistent with the direction of the observed spontaneous polarization.

Most intriguing in TbMn_2O_5 is the multiple contributions to the spontaneous polarization. When the Tb^{3+} moments are aligned along the a axis by a magnetic field, the contribution of Tb^{3+} sites are suppressed. This causes a dramatic effect of magnetic-field driven polarization reversal at low temperature (Chapon *et al.*, 2004; Hur *et al.*, 2004), although the effect is volatile.

Orthorhombic RFeO_3 (R =rare earth and Y)

Rare earth ferrites RFeO_3 crystalize in orthorhombic structure (Maezio *et al.*, 1970), similar to other rare-earth (R) transition-metal (M) RMO_3 compounds, where $M = \text{Sc-Ni}$ (Xu and Wang, 2014). For RFeO_3 , the magnetic transition temperature T_N below which Fe^{3+} moments order is high ($> 600\text{K}$) (Treves, 1965; White, 1969; Cheremisinoff, 1990), similar to that of BiFeO_3 . When R^{3+} ions are magnetic, their moments order at a much lower ($< 10\text{K}$) temperature (Rado and Suhl, 1963). The strong lattice distortion in the Pbnm structure, especially the rotation and tilt of the FeO_6 octahedra complicate the spin structures.

Right below T_N , RFeO_3 adopts a $G_xA_yF_z$ (the Bertaut notation) (Rado and Suhl, 1963) spin structure for Fe^{3+} , as shown in Fig. 11(a), where G_x , A_y , and F_z denote the G-type arrangement for the x component, A-type for the y component, and ferromagnetic alignment for the z component of the spins respectively. In this case, the DM interaction generates a tilt of the Fe^{3+} moments along the c axis (Fig. 11(b)), making RFeO_3 weakly ferromagnetic with a moment on the order of $0.1 \mu_B/\text{Fe}$ (Gorodetsky *et al.*, 1966).

In DyFeO_3 , the Dy^{3+} moments form the G_xA_y order below about 3.5K , while the Fe^{3+} moments becomes $A_xG_yC_z$ without the weak ferromagnetic order. A magnetic field along the c axis restores the $G_xA_yF_z$ order for the Fe^{3+} moments and makes DyFeO_3 ferroelectric (Tokunaga *et al.*, 2008). A projection of this spin structure onto the a - c plane is shown in Fig. 11(c), in which the $\uparrow\uparrow\downarrow\downarrow$ spin structure and the dimer pairs of Fe^{3+} moments and R^{3+} moments can be identified. Due to the exchange striction (see Section “Exchange striction”), this dimerization generates a polarization along the c axis in DyFeO_3 (Tokunaga *et al.*, 2008). Thus, DyFeO_3 exhibit the magnetic-field induced ferroelectricity.

In GdFeO_3 , the magnetic order is G_xA_y for Gd^{3+} moments and $G_xA_yF_z$ for the Fe^{3+} moments below about $T_N(\text{Gd}) \approx 2.5\text{K}$, which allows for the spontaneous polarization and ferroelectric order (Tokunaga *et al.*, 2009). More interesting is the effect of the electric and magnetic fields. With a magnetic field along the c axis, net magnetization which comes from the Fe^{3+} moments can be reversed. Unfortunately, the reversal of polarization is not observed in GdFeO_3 , suggesting that the Gd^{3+} moments follow the Fe^{3+} moments. Similarly, an electric field along the c axis can reversal the polarization, but no reversal of magnetization is observed, suggesting that it's Gd^{3+} moments that reverses when the dimerization pattern changes. Nevertheless, substantial change of polarization and magnetization in the magnetic field and in the electric field are found, which is attributed to the nucleation of composite domains that allows multiple switching routes (Tokunaga *et al.*, 2009).

Obviously, the key to realize electric-field-driven and magnetic-field-driven reversal of magnetization and polarization respectively is to enhance the anisotropy energy of R^{3+} , making them more difficult to reverse. This has been achieved with $R = \text{Dy}_{0.7}\text{Tb}_{0.3}$ with fast switching at 2.5K (Tokunaga *et al.*, 2012). The non-volatility of the effect is especially appealing.

Magnetoelectric Effects

Basis Aspects of Magnetoelectricity

The linear magnetoelectric effect describes a phenomenon by which magnetization, M , (polarization, P) is induced in a material on exposure to an electric E -field (magnetic H -field). The linear response of the material on the applied fields is mediated by the magnetoelectric susceptibility $\alpha_{ij} = \mu_0 \partial M_i / \partial E_j = \partial P_i / \partial H_j$. For α_{ij} to be non-zero, time reversal and spatial inversion symmetry have to be broken while their combined application leaves the system invariant. In multiferroics, magnetic long range order breaks time

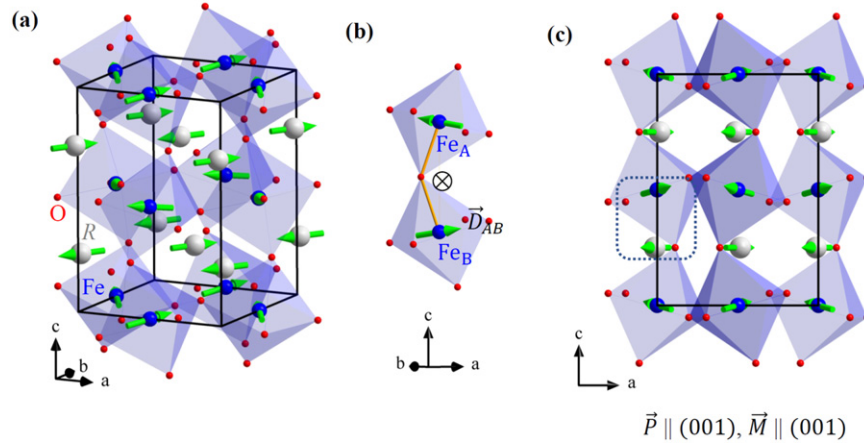


Fig. 11 Orthorhombic $R\text{FeO}_3$. (a) A spin structure $G_x A_y$ for the R^{3+} moments and $G_x A_y F_z$ for the Fe^{3+} moments. (b) Schematics for the canted Fe^{3+} moments from the DM interaction. (c) Projection of (a) on the a - c plane highlighting the dimerization of spins in the box of dashed lines.

inversion symmetry while ferroelectric order breaks inversion symmetry. This makes multiferroics strong candidates for materials with magnetoelectric coupling and magnetoelectric response. However, the presence of multiple ferroic orders is not the only pathway towards magnetoelectricity. In fact, the linear magnetoelectric effect was first predicted and experimentally verified for the rhombohedral antiferromagnet $\alpha\text{-Cr}_2\text{O}_3$ (Landau and Lifshitz, 1960) where antiferromagnetic order is the only spontaneous ferroic long range order in the material.

In the archetypical magnetoelectric $\alpha\text{-Cr}_2\text{O}_3$, the magnetoelectric susceptibility tensor α_{ij} is diagonal with tensor elements $\alpha_{\parallel}$ and $\alpha_{\perp}$ for responses parallel and perpendicular to its trigonal crystal axis (H O'Dell, 1970). In a modern view on magnetoelectricity, the magnetoelectric susceptibility tensor is often considered in terms of multipolization, i.e., a decomposition of α_{ij} which, in the case of Cr_2O_3 , is a decomposition into a trace free and a pseudoscalar component. In the context of multipolization, the trace free tensor component is known as quadrupole and the pseudoscalar or axion piece is known as monopole contribution (Spaldin, 2021). The presence of a monopole contribution to the magnetoelectric response in Cr_2O_3 is remarkable. The existence of such a contribution was long debated mainly due to the notion of a Post constraint (Post, 1997). More recently, the existence of a monopole or pseudoscalar response has been unambiguously confirmed (Hehl et al., 2009) and it is also present in topological insulator materials with a topological magnetoelectric effect. The latter appears when the time inversion symmetry of a topological insulator thin film is weakly broken by adjacent top and bottom magnetic thin films with opposite orientation of the magnetization of the top and bottom films (Pournaghavi et al., 2021). In addition to quadrupole and monopole components, the magnetoelectric response of a system can contain a toroidal moment when the susceptibility tensor differs from the diagonal structure of $\alpha\text{-Cr}_2\text{O}_3$.

The archetypical magnetoelectric Cr_2O_3 provides a simple and intuitive microscopic mechanism for parallel magnetoelectric response. Fig. 12(a) shows a fraction of the unit cell of $\alpha\text{-Cr}_2\text{O}_3$ which, for simplicity, displays only two Cr^{3+} -ions of the otherwise four representative ions necessary to display the antiferromagnetic order parameter. The two displayed ions have opposite spins. They are aligned along the crystallographic c -axis, which is a 3-fold symmetry axis of the crystal. In zero applied electric field, the Cr^{3+} -ions of opposing spin orientation experience identical crystal fields within their slightly distorted O^{2-} octahedral environments. The small parameter, δ , depicts that there is a difference in the size of the two O^{2-} triangles which, for $\delta = 0$, would form a perfect octahedral environment. In the presence of an electric field applied along the c -axis (see Fig. 12(b)), the Cr^{3+} -ions are slightly displaced from their equilibrium positions. Their shift along the c -axis into new positions (ion A moves towards the larger and ion B towards the smaller triangle) lifts the degeneracy of the sublattice magnetization due to dissimilar change in the crystal field environment of the surrounding O^{2-} ions. The sublattice magnetizations no longer fully compensate and a small magnetic moment, $\mu_0 M_3 = \alpha_{\parallel} E_3$ emerges. The magnitude of the parallel susceptibility, $\alpha_{\parallel}$, peaks near the Néel temperature of $T_N = 307\text{K}$ at a value of about 4 ps/m .

The phenomenology of the linear magnetoelectric effect, $\mu_0 M_i = \alpha_{ij} E_j$, can be understood in terms of a free energy, $G_{\text{IME}} = -\alpha_{ij} H_i E_j$, which contributes to the total Gibbs free energy of a system. G_{IME} allows an intuitive interpretation as Zeeman energy which the electrically induced moment experience in the applied magnetic H -field. G_{IME} is a leading term in a more general expansion of the Gibbs free energy in terms of E and H which reads (Fiebig, 2005; Kleemann and Binek, 2013)

$$G(E, H) = G_0 - \frac{1}{2} \epsilon_0 \chi_{ij}^e E_i E_j - \frac{1}{2} \mu_0 \chi_{ij}^m H_i H_j - \alpha_{ij} H_i E_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k - \frac{1}{2} \delta_{ijkl} E_i E_j H_k H_l$$

with χ_{ij}^e , χ_{ij}^m , and α_{ij} being the linear electric, magnetic, and magnetoelectric susceptibility tensors, and β_{ijk} , γ_{ijk} and δ_{ijkl} being the tensors of non-linear magnetoelectric response. Note that the free energy expression assumes Einstein's summation convention. The linear magnetoelectric susceptibility has an upper bound (Brown et al., 1968) given by $\alpha_{ij}^2 < \frac{1}{c^2} \chi_{ii}^e \chi_{jj}^m$, showing that the linear magnetoelectric effect is relativistically small. The non-linear magnetoelectric contributions are even smaller for typical laboratory fields, however the symmetry prerequisites are less stringent.

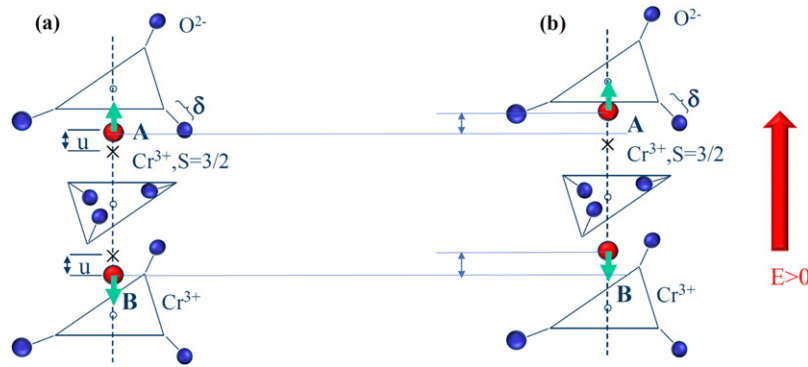


Fig. 12 (a) Fraction of the magnetic unit cell of Cr_2O_3 illustrating antiferromagnetic alignment of spins (up and down arrows) along the c -axis associated with the Cr^{3+} ions (red spheres). Cr^{3+} ions are surrounded by O^{2-} ions (blue circles) forming a distorted octahedral crystal-field environment. The parameter δ indicates slightly different sizes of O^{2-} triangles. The parameter u indicates position of Cr^{3+} ions relative to the middle points between O^{2-} triangles marked by crosses on the c -axis. (b) Fraction of the magnetic unit cell of Cr_2O_3 emphasizing the change of the position of Cr^{3+} ions in the presence of an applied electric field, E , applied along the c -axis. Ion A with spin up is displaced from its equilibrium position in $E = 0$ towards the larger O^{2-} triangle. Ion B with spin down is moving towards the smaller O^{2-} triangle. Amount of the ion shifts are indicated by spacing between horizontal lines.

Magnetoelectricity in Multi-Phase Composites

So far our main focus has been on multiferroics and magnetoelectric single phase materials. However, record breaking magnetoelectric response is observed in composite multiferroics with ferroelectric (or piezoelectric without ferroelectric long range order) and ferromagnetic materials in close proximity (Nan *et al.*, 2008) which allows for stress-strain coupling (Wang *et al.*, 2010). Two phase multiferroics or multiphase laminates owe their magnetoelectric effect to the coupling between the piezoelectric response of the piezoelectric component of the composite which strains the adjacent ferromagnetic. Prominent examples include the archetypical $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$ composite which exceeds, *e.g.*, the magnetoelectric response of Cr_2O_3 by two orders of magnitude (van Suchtelen, 1972). The ferromagnetic component changes its magnetization due to a magnetoelastic effect which originates from spin-orbit coupling in the material. Note that ferroelectrics often serve of piezoelectric components because all ferroelectrics are piezoelectric while not all piezoelectric materials are ferroelectric. The stress-strain coupling and the resulting magnetoelectric response, α , can be intuitive summarized as (Nan, 1994)

$$\alpha = \frac{\text{magnetic response}}{\text{electric stimulus}} = \frac{\text{magnetic response}}{\text{mechanical stimulus}} \times \frac{\text{mechanical response}}{\text{electric stimulus}}$$

More recently, composites and laminates evolved into nano thin film heterostructures with record breaking magnetoelectric response. Multiphase composites find applications as field sensors, memory devices and antennas (Wang *et al.*, 2014). For sensor and antenna applications in particular, optimization of materials properties focuses on the minimization of dielectric losses and maximization of piezoelectric and magnetoelastic coefficients of the constituent materials in frequency ranges specific to their applications (Shevlin, 2019). The magnitude of the magnetoelectric response depends strongly on the frequency of the applied stimulating field and resonances have to be exploited.

Magnetoelectric Switching

Applications such as magnetoelectric memory devices depend on the ability to switch a ferroic order. Switching is ideally non-volatile, with energy-efficiency aiming at atto/switch and THz switching speed. The linear magnetoelectric effect does not per se warrant non-volatile switching of a ferroic order. Switching is a non-linear phenomenon. However, in systems such as the linear magnetoelectric antiferromagnets, the linear magnetoelectric effect provides an energy imbalance between antiferromagnetic single domain states of opposite orientation of the Néel vector and consequently opposite sign in the magnetoelectric response. Switching is achieved when the free energy difference between two domain states, $\Delta G_{\text{IME}} = -2\alpha_{ij}H_iE_j$, overcomes the magnetic anisotropy energy (Martin and Anderson, 1966). In single phase multiferroics with sizable order parameter coupling, switching of the ferroelectric polarization can give rise to non-volatile switching of the magnetic order parameter which can be utilized either directly or indirectly via exchange bias to set a state variable in a memory device (He *et al.*, 2010; Wu *et al.*, 2013; Dowben *et al.*, 2016) The fact that magnetoelectric memory devices allow to switch the state variable by voltage application in the absence of electric currents makes them candidates for energy-efficient post CMOS device applications (Vedmedenko *et al.*, 2020).

Future Directions

The fundamental understanding gained from studying multiferroics in the past few decades, will continue guiding the search and design for single-phase multiferroic materials of more ideal properties, *i.e.*, high ferroic ordering temperatures and strong magnetoelectric couplings (Lu *et al.*, 2019). More novel physical properties are expected from the domain walls, where the symmetry of charge, structure, and spin are distinct from that of the bulk (Choi *et al.*, 2010; Farokhipoor *et al.*, 2014; Leo *et al.*, 2018; Evans *et al.*, 2020). In addition, the physical phenomena discovered in multiferroics, beyond electric-control of magnetism, are benefiting other fields, such as photovoltaics (Choi *et al.*, 2009) and photocatalysis (Gao *et al.*, 2015). The microscopic model built to analyze multiferroics also found connection to high energy physics and cosmology (Wilczek, 1987; Spaldin, 2017a).

The future of magnetoelectric materials science is almost certainly driven by applications notably memory, sensing, and antennas. The critical need for energy-efficient and ultra-fast post CMOS devices will continue to be a driver of the field. The promise of pure voltage controlled non-volatile antiferromagnetic spintronics is within reach with many variations of magnetoelectric random access memory and logic devices under investigation (Binek and Doudin, 2005; Chen *et al.*, 2006; Manipatruni *et al.*, 2019; Dowben *et al.*, 2020). Recently, the archetypical magnetoelectric material Cr_2O_3 and its boron doped variation B: Cr_2O_3 saw exciting new developments with the investigation of potentially voltage-controlled spin dependent transport in graphene in proximity of the magnetoelectric antiferromagnet (He *et al.*, 2022) and the demonstration of B: Cr_2O_3 as a single phase material which allows non-volatile reorientation of the Néel vector in the absence of an applied magnetic field and at temperatures compatible with CMOS environments. (Mahmood *et al.*, 2021) The absence of ferromagnetic order in voltage-controlled antiferromagnetic spintronics is particularly appealing for ultra-fast (THz) switching.

The quantized topological magnetoelectric effect and its relation to the quantum anomalous Hall effect will remain subject to fundamental investigations. The relation between the topological magnetoelectric effect and the presence of a magnetoelectric monopole response in topologically trivial antiferromagnetic magnetoelectric insulator enables exciting realizations of axion electrodynamics (Wilczek, 1987; Essin *et al.*, 2009) They will increasingly become subject of experimental investigation. They have implications and analogies in high energy physics where axions are candidates for dark matter and a possible solution for the strong CP problem (Kim, 1987).

Recent advances in two dimensional magnetic materials spark interest in two dimensional multiferroics and magnetoelectrics in single phase materials as well as multiferroic heterostructures (Zhong *et al.*, 2020; Ying and Zülicke, 2022).

Conclusions

The past decades have seen the studies on multiferroics evolve from “ferroelectromagnets”, focusing on coexisting electric and magnetic orders, to “magnetoelectric multiferroics”, aiming more on understanding and application of the magnetoelectric couplings. In fact, the flurry of efforts demonstrated abundant new phenomena way beyond magnetoelectric effects. While multiferroics with strong magnetoelectric coupling continue to be an exciting field which allows to address a plethora of fundamental questions and helps overcoming roadblocks in information technology and sensing, other related phenomena will also keep attracting attention for more comprehensive understandings.

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Spin Orbit Torque Based Devices: Concepts, Progress, and Perspectives

Chang-Ming Hung, Amit Chanda, Hari Srikanth, and Manh-Huong Phan, Department of Physics, University of South Florida, Tampa, FL, United States

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Abstract

Spin orbit torque (SOT) provides a novel platform for the electrical manipulation of magnetization in spintronic devices - the key components in computing systems. This article discusses basic concepts, recent progress, and future perspectives for SOT-based devices. After a brief introduction of the magnetoresistive random-access memory (MRAM) technology, the fundamental aspects of SOT and associated characterization techniques are described. A wide range of SOT materials is assessed, which highlights a new, promising perspective for modern SOT devices based on two-dimensional (2D) van der Waals (vdW) materials and heterostructures. Our review will stimulate further research in this rapidly expanding and exciting research field.

Introduction

Nowadays, the need for ultra-fast computing and data storage has increased drastically. General computing systems contain several levels of memory storage places for effectively processing data. [Fig. 1](#) illustrates the memory hierarchy. Starting from the core, the central processing unit (CPU), the brain of a computer, calculates and operates the whole system but has a limited storage space. To resolve the limitation of space in the CPU, high-speed caches such as static random-access memory (SRAM) are used to follow the high-speed operations in the CPU. SRAM is a volatile memory, which means that data will not be stored without power supply. A lower level of memory is called dynamic random-access memory (DRAM). DRAM acts as the main memory and has a larger storage space but a higher power consumption (constantly supplying power to keep memory retention) and a lower speed compared to SRAM. The lowest storage levels are the solid-state drives (SSD) and the hard disc drives (HDD) which have the slowest writing/reading speed. In the memory hierarchy, there are operating speed gaps between SRAM (less than 1 ns) and DRAM (around 30 ns) and HDD (around 10 ms) ([Kent and Worledge, 2015](#)). In addition, SRAM has a higher manufacturing cost, and requires a complex lithography process. Furthermore, both DRAM and SRAM are volatile. Therefore, it is necessary to find potential candidates that have high writing/reading speed, low energy consuming, and cost-effective straightforward fabrication process. To address these issues, the spin transfer torque- magnetic random-access memory (STT-MRAM) has been proposed toward the next generation of memory devices. To fully understand the potential applications of STT-MRAM, it is imperative to understand the history of MRAM.

MRAM can be traced back to the discovery of giant magnetoresistance (GMR) by Albert Fert ([Baibich et al., 1988](#)) and Peter Grünberg ([Binasch et al., 1989](#)) for which they won the Nobel prize in 2007. Multilayer structures with spin dependent scattering, causes a GMR difference when the magnetic moments of the adjacent magnetic layers are aligned parallel or antiparallel to each other. Hence, GMR opens a huge number of applications such as magnetic field sensors ([Reig et al., 2009](#)), HDD, micro-electro-mechanical system ([Guedes et al., 2012](#)) (MEMS), and MRAM ([Guedes et al., 2012](#)). Giant room temperature tunneling magnetoresistance (GTMR) was discovered in 1995 ([Moodera et al., 1995](#)). In 1996, Slonczewski proposed STT switching ([Slonczewski, 1996](#)). Then further enhancement of the magnetoresistance was observed by changing the tunneling barrier from AlO_x to MgO in 2004 ([Parkin et al., 2004](#)). The single-crystalline Fe/MgO/Fe magnetic tunneling junction (MTJ) showed a giant tunneling magnetoresistance (TMR) ratio up to 180% at room temperature, which was attributed to the coherent spin-polarized tunneling (non-zero density of states for the majority spin band but nearly zero density of states for the minority spin band), in which the symmetry of electron wave functions plays a crucial role ([Yuasa et al., 2004](#)). In 2010, Hideo Ohno proposed the perpendicular magnetic tunneling junction (PMTJ) based on CoFeB , which made it possible to combine all the desired characteristics of a high-density non-volatile memory at the same time in a single device: the high thermal stability at reduced dimension (40 nm), low-current (49 μA)-induced magnetization switching and high TMR ratio (120%) ([Ikeda et al., 2010](#)). Notably, the traditional MRAM device needs an external magnetic field, which limits the possibility of reduced dimensionality ([Bhatti et al., 2017](#)), whereas STT-MRAM can eliminate the need for field assisted switching and can change its free layer magnetization based on the writing current directions ([Bhatti et al., 2017](#)). Furthermore, the reading and writing times for the STT-MRAM are in the range of 2 to 30 ns, making it a perfect fit in the speed gap between SRAM and DRAM. However, STT-MRAM has some drawbacks. STT based MRAM is composed of two terminal structures where the writing and reading processes occur in the same lines. When the writing current passes through tunneling barriers, higher power consumption is needed to switch the magnetization. Hence, it comes with thermal instability problems and back-hopping behavior in some of the STT-MRAMs ([Tang and Pai, 2020](#)). Moreover, the writing current pulse has the possibility to damage the tunneling barrier which leads to lifetime and reliability issues.

In order to understand the spin orbit torque (SOT) based MRAMs (SOT-MRAMs) further, it is necessary to understand the basic STT-MRAM switching mechanism. The STT-MRAM structure is composed of an MTJ, which contains a magnetic free layer (FL)/tunneling barrier/ magnetic pinned layer (PL) ([Kawahara et al., 2012](#)). Here, the writing and reading processes occur separately. As mentioned earlier, the STT-MRAM is a two-terminal structure. For the reading process, a small reading current passes from one side of terminal toward the MTJ structure. When the FL and the PL have the same magnetization direction (parallel), the measured resistance would be low and vice versa. For the writing process, there are two different scenarios regarding the relative orientation of the magnetization of the FL and PL, which are either parallel (P) or anti-parallel (AP). (1) For the AP mode to P mode: the electrons flow from PL to FL. When

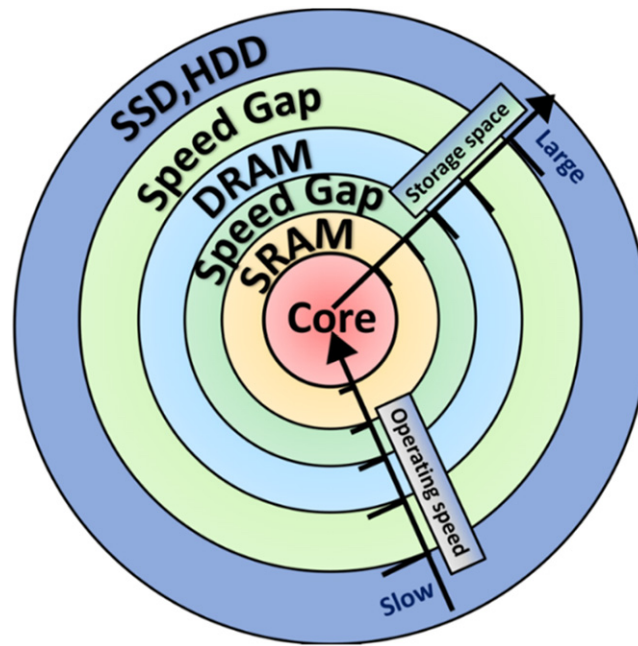


Fig. 1 The historical development of memory technologies (memory hierarchy).

electrons flow through the PL, the spins with the direction of polarization parallel to that of the PL would pass through barrier towards and insert STT to FL and change it to P mode when the sourcing current is large enough. (2) For the P mode to AP mode: the electrons go from FL to PL. When electrons pass through FL, the electron spins with the direction of polarization parallel to the magnetization direction of the FL will pass through to PL but the spins with the direction of polarization anti-parallel to the magnetization direction of the FL would bounce back to the FL and change the magnetization in the FL based on the SIT mechanism.

SOT has gathered more interests around 2012 (Liu *et al.*, 2012b). The basic structure of SOT-MRAM is different from that of STT-MRAM as SOT-MRAM has three terminal structures, since the writing and reading paths are separated. Separating the paths largely reduces the energy needed to switch the magnetization, and current pulses would not directly pass through MTJ which eliminates the damage of the MgO insulating tunnel barrier. SOT and related topics have been an active research area in the field of magnetism and spintronics. Fig. 2 shows an increasing trend in SOT-related research (the data were collected from 2000 till the end of October 2022). In this article, we provide a brief review of basic concepts and recent advances in SOT, as well as future perspectives for SOT devices. Given the recent discovery of two-dimensional (2D) van der Waals intrinsic magnets that exhibit outstanding optoelectronic and magnetooptical properties, these 2D materials become competitive candidates for SOT-MRAM technology. The article starts with a brief historical introduction to the MRAM technology, followed by a description of the basic SOT concepts and characterization techniques. A wide range of SOT materials is then reviewed, with an emphasis on the recent exploration of 2D van der Waals materials for SOT devices. Concluding remarks and future perspectives are finally made.

Fundamentals of Spin-Orbit-Torque (SOT)

Concepts and Mechanisms

Spin orbit torque (SOT) is based on the “spin current” to manipulate the magnetization. The origin of SOT comes from spin Hall effect (SHE) and Rashba effect, which can generate spin current from the sourcing charge current (Fig. 3).

However, we should understand more about “the Hall effect family” before we consider the SHE. Everything begins in 1879, when Edwin Hall found transverse voltage can be measured when an out of plane external magnetic field is applied orthogonal to the charge current direction in normal metals or semiconductors. This effect is called the ordinary Hall effect (OHE) (Hall, 1879). The OHE is basically the result of the Lorentz force acting on the charge carriers and depends on the carrier density and mobility. In 1881, Hall tried to measure the Hall resistance of a ferromagnetic (FM) metal (Hall, 1880). The resistance measured is ten times larger than normal metal case and named it as anomalous Hall effect (AHE). Later, the empirical relation is built: $\rho_{xy} = R_0 B + R_S \mu_0 M$, where R_0 , R_S , B , μ_0 and M are ordinary Hall coefficient, anomalous Hall coefficient, magnetic field, permeability of free space, and magnetization, respectively. This equation indicates that the resistivity has a contribution from the OHE and the AHE. Based on the origins of the AHE, they can be divided into intrinsic and extrinsic contributions. Intrinsic contribution comes from Berry curvature (Xiao *et al.*, 2009) and extrinsic contribution comes from the skew scattering and side jump mechanisms (Nagaosa *et al.*, 2010). When charge current passes through FM metal in the longitudinal direction, the electrons

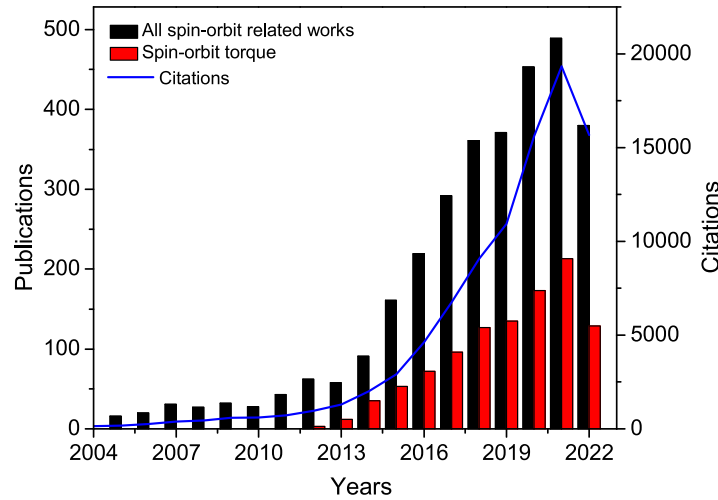


Fig. 2 Publications and citations per year in the spin-orbit related research areas. The data were collected from Web of Science with “spin orbit torque” or “spin orbit” as a keyword.

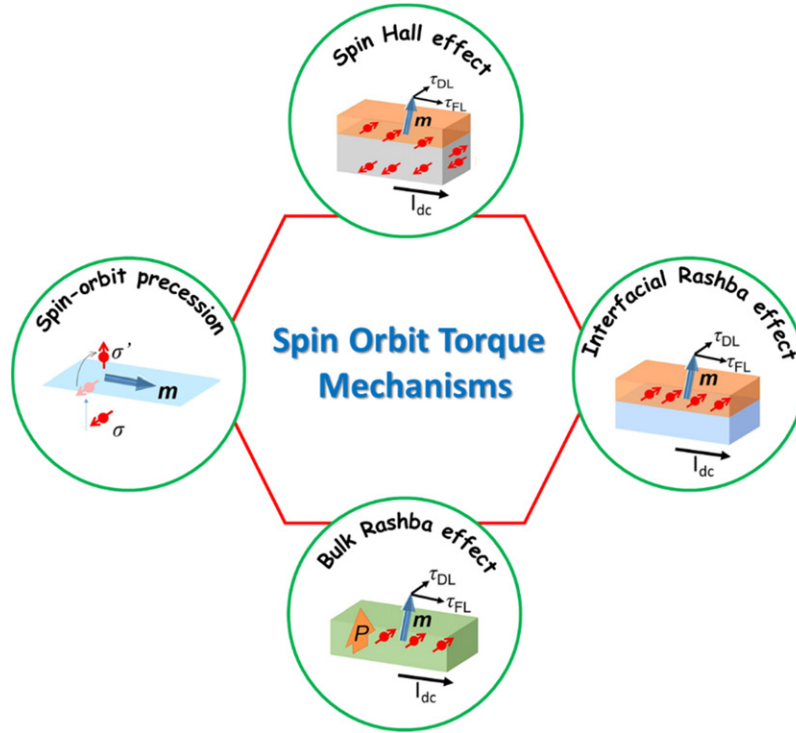


Fig. 3 Schematics for spin orbit torque (SOT) mechanisms.

experience the transverse velocity which separates the spin-up and spin-down electrons. In addition, in FM metal, the majority and minority spins are unequal which means that there is an imbalance in the accumulation of electrons with opposite spin directions, which gives rise to an additional “anomalous” voltage signal to the ordinary Hall signal. The anomalous Hall resistivity is proportional to the magnetization of FM metal (as the empirical relation showed earlier in the paragraph) and hence it can also be used to probe the magnetization of a FM metal.

In 1999, the spin Hall effect (SHE), named by Hirsch (Hirsch, 1999), was proposed. The SHE is also a spin dependent scattering mechanism but shows in normal nonmagnetic metals. When charge current passes through a normal metal, spin current is generated in the transverse direction. However, in the absence of an applied magnetic field, the transverse voltage is zero, since the flows of spin-up and spin-down electrons cancel each other. The correlation between charge current and spin current based on SHE can be interpreted as: $\mathbf{j}_s = \left(\frac{\hbar}{2e}\right)\theta_{SH}(\hat{\sigma} \times \mathbf{j}_c)$, where $\mathbf{j}_s$, $\mathbf{j}_c$, $\hat{\sigma}$, and θ_{SH} represented as spin current, charge current, spin polarization vector, and spin Hall angle, respectively. From experimental point of view, SHE was first measured through Kerr imaging in a semiconductor,

gallium arsenide, GaAs (Kato *et al.*, 2004). Later, 5d heavy transition metals such as: Pt (Skowroński *et al.*, 2019) and β -W (Cao *et al.*, 2020; Pai *et al.*, 2012) have relatively large atomic numbers and have been widely used for spintronics applications. Since the origin of SHE is also spin dependent scattering, three mechanisms mentioned above in AHE are also similar here: spin skew scattering, side jump mechanism and Berry curvature. In 1958, Smit proposed skew scattering to explain origin of the AHE (Smit, 1958). Skew scattering originates from scattering centers which carry a gradient effective magnetic field, due to the spin orbit coupling. When electrons carry different orientations of spins, they experience a force (forward or reverse) with respect to the scattering center. For the side jump (Berger, n.d.) mechanism, it is due to multiple scattering mechanisms from impurities. This spin dependent scattering would rather accelerate or decelerate and hence it results the separation of the spins with different orientations. The intrinsic mechanism is originally proposed by Karplus and Luttinger (1954). In a ferromagnetic metal/semiconductor, when an electron moves through a periodic potential with strong spin-orbit coupling, it acquires an additional “anomalous group velocity” driven by an electric field related to the “Berry phase curvature” which mainly originates from the “unconventional” variation of the Bloch state in the momentum space due to its inherent topological properties. This anomalous group velocity drives the spin up and spin down electrons in the opposite directions and hence separates their paths which eventually gives rise to the AHE.

On the other hand, systems with broken inversion symmetry can also generate spin current, this effect is named as the Rashba-Edelstein effect (Koo *et al.*, 2020; Manchon *et al.*, 2015). Rashba spin orbit coupling shifts the degenerate spins towards the momentum direction. When electric field applied, the Fermi surface offsets from the center and hence spins are accumulated. Typical SOT based device configurations contains FM/HM, and therefore inversion symmetry breaks in the interface. Due to the interfacial electrical field ($E = E_z$), the spins can be accumulated at the interface. Besides the interfacial Rashba-Edelstein effect, the bulk Rashba effect or the so-called Dresselhaus effect can also play a role in contributing to the spin torque efficiency. The bulk Rashba effect comes from the broken bulk inversion symmetry and the Dresselhaus spin-orbit coupling (Ishizaka *et al.*, 2011; Jeon *et al.*, 2021). In addition, both the Dresselhaus and interfacial Rashba effect cause the spin momentum locking. Zinc blende type systems, such as dilute magnetic semiconductors (Ga,Mn)As, are the typical bulk symmetry broken materials which can reach single layer spin orbit torque switching (Jiang *et al.*, 2019; Park *et al.*, 2021).

When extending the concept from the interfaces toward three-dimensional (3D) systems, other spin current contributions can also arise. When the electron spin passes through the interface of a heterostructure, the interfacial spin orbit effective field, such as Rashba spin orbit field, will result in the spin filtering effect (Amin *et al.*, 2018). Electron spin alignment with the spin orbit field direction will have a high possibility of transmission and vice versa. Spin-orbit precession can occur during the electron spin's transmission which is not collinear to the spin orbit field, and the electron spin processes according to the interfacial spin orbit field and allows different directions of spin polarization (Amin *et al.*, 2018).

Another important interfacial effect should also be addressed here. The Dzyaloshinskii-Moriya interaction (DMI) is an asymmetric exchange interaction that happens when system combines spin orbit coupling and inversion symmetry breaking in a non-centrosymmetric system or interface (Dzyaloshinskii, 1964; Moriya, 1960). DMI can be described as energy term: $E_{DMI} = D_{12} \cdot (S_1 \times S_2)$ where D is the Dzyaloshinskii-Moriya vector and $S_{1,2}$ are the neighboring spins. The existence of DMI stabilizes the chiral spin textures and causes various interesting phenomena such as skyrmions (Fert *et al.*, 2017) and the topological Hall effect (THE) (Lee *et al.*, 2020; Parkin *et al.*, 2020). From the SOT point of view, DMI stabilizes Néel type domain walls in PMA systems, which reduces processing time. However, stronger DMI requires higher in-plane bias field to depin the domain walls.

Landau-Lifshitz-Gilbert-Slonczewski Equation

To understand the writing process, the spin dynamics can be described by the Landau-Lifshitz-Gilbert-Slonczewski (LLGS) equation based on a macrospin model: $\frac{dm}{dt} = -\gamma m \times H_{eff} + \alpha m \times \frac{dm}{dt} - \tau_{FL} m \times \hat{\sigma} - \tau_{DL} m \times (m \times \hat{\sigma})$, where m , γ , H_{eff} , α , τ_{FL} , and τ_{DL} are magnetization, gyromagnetic ratio, effective magnetic field, Gilbert damping, field like torque, and damping like torque, respectively. The first term represents the precessional term, and the second term describes the dissipative damping. The last two terms in the LLGS equation are related to current induced spin torques. In systems with perpendicular magnetic anisotropy (PMA), the damping like torque and field like torque generate an out-of-plane damping like effective field (H_{DL}) and in-plane field like effective field (H_{FL}) in accordance to the expression: $\tau_{DL,FL} \propto m \times H_{DL,FL}$.

Switching Mechanism

To achieve deterministic magnetization switching, HM/FM bilayer systems are required to break the inversion symmetry. Although, inversion symmetry breaking generally happens in typical bilayer structures due to interface between two different layers, the Rashba effect is generally not the main mechanism to reach a complete SOT switching. Hence, we mainly discuss the switching concept based on the SHE below.

Let us assume that the charge current passes through the positive x -axis and the magnetization is pointing up (a sample with PMA properties illustrated in Fig. 4a). When the mirror plane is along the xz direction, charge current would not change its direction but the magnetization will change its direction on the other side of the mirror. Charge current with a spatial vector parallel to the mirror plane would not change the direction on the other side of mirror. However, the magnetization acts as a pseudo-vector parallel to the mirror plane and changes its direction on the opposite side of the mirror. According to the formula for H_{DL} and H_{FL} which corresponds to τ_{DL} and τ_{FL} , H_{DL} would point along the x -axis, but H_{FL} would be orthogonal to the mirror

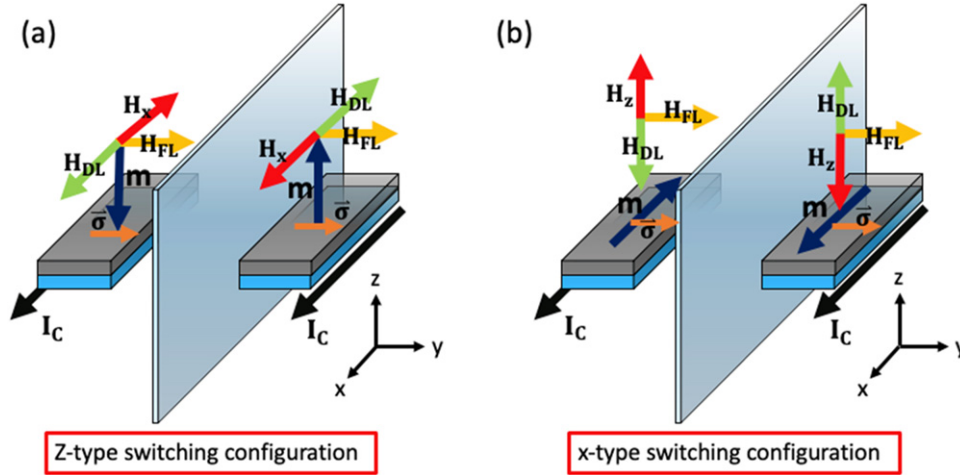


Fig. 4 (a) Z-type and (b) X-type SOT switching configurations.

plane (along the y -axis). Since the effective field is also a pseudovector, H_{DL} has opposite direction on the other side of mirror, but H_{FL} remains the same direction, since it is perpendicular to the mirror plane. As a result, charge current applies along the positive x -axis but it allows two magnetization states to happen at the same time, which means it would not reach magnetization switching. Therefore, the application of an external magnetic field along the charge current direction is necessary to break the mirror symmetry and accomplish deterministic switching.

Besides PMA systems denoted as z -type SOT switching, there are also two other types of switching, x -type and y -type SOT switching according to the system's easy axis direction. In the case of y -type switching, it is similar to the STT-type switching as it breaks the symmetry. The y -type switching starts from a thermal activation process and needs a longer pulse width, and the switching process often accompanies with lots of precessions. Therefore, the total switching time is relatively longer compared to the z -type and x -types. On the other hand, the x -type SOT switching needs an external magnetic field applied along the z -direction to break the switching and reach deterministic switching as illustrated in Fig. 4b (Fukami *et al.*, 2016).

Zero Field Switching

From the application point of view, the assistance of an external magnetic field is not feasible since it limits the single bit size. Therefore, several solutions have been proposed which can break the mirror symmetry and achieve field-free switching. The methods listed here are based on the z -type SOT switching and shown in Fig. 5. (1) Asymmetric structures break mirror symmetry. Yu *et al.* (2014) proposed $\text{Ta}/\text{Co}_{20}\text{Fe}_{60}\text{B}_{20}/\text{TaO}_x$ with a wedge structure on the TaO_x side and this gradient in the TaO_x layer generates an extra in-plane charge current, which allows extra OOP H_{FL} . Interestingly, wedged W in the Pt/W/FM systems can also reach zero-field switching (Chen *et al.*, 2019). (2) Build-up exchange bias (EB) by the insertion of an antiferromagnetic (AFM) layer. EB is a method that can "pin" the interfacial FM spin by training with a field above the Néel temperature (T_N) of the AFM layer. When the EB field is along the charge current direction, the tilted interfacial spin offers an effective external field to break the mirror symmetry. Fukami *et al.* showed that $\text{Ta}/\text{PtMn}/[\text{Co}/\text{Ni}]_2/\text{Co}/\text{MgO}/\text{Ta}$ reached zero-field switching by utilizing the EB between PtMn and Co (Fukami *et al.*, 2016). (3) The T -type SOT switching is utilized by including a PMA layer and an IP magnetic layer. Kong *et al.* proposed $\text{MgO}/\text{CoFeB}/\text{Ta}/\text{CoFeB}/\text{MgO}$ with one CoFeB PMA and one CoFeB IP magnetization. The stray field between the two layer's magnetization offers an extra bias field (Kong *et al.*, 2019). Hence, the structure reached robust zero field switching. (4) Gradient stacking magnetic layers combined with gradient DMI; For example, ultra-thin $\text{Co}_{1-a}\text{Tb}_a$ layers with composition gradient were stacked together and hence the symmetry breaks along the growing direction. In addition, the rare-earth metal, Tb, possesses large spin orbit coupling and acts as a spin current source which eliminates the need for an extra single HM layer to generate spin current (Zheng *et al.*, 2021). (5) Gradient of spin current through an extra ferroelectric layer has been proposed in a PMN-PT/Pt/FM stack (Cai *et al.*, 2017). This is based on the SHE generated spin current and the spin orbit field due to the electrical polarization of the PMN-PT interface with Pt. Similar to the wedge structure, the out-of-plane interfacial electrical field difference, generated by an extra spin current, allows zero-field switching. Besides the z -type, the x -type can easily reach field-free switching by slightly canting the easy axis angle (Liu *et al.*, 2021a,b).

Characterization Techniques

Based on the in-plane or out-of-plane easy axis of the magnetic layer, there are different basic ways to characterize SOT and the device efficiency including electrical and optical characterizations (Fig. 6). In PMA systems, SOT can be measured by direct switching, hysteresis loop shift measurements (Pai *et al.*, 2016) and second harmonic Hall voltage measurements (Hayashi *et al.*, 2014). In IP systems, SOT can be characterized by the differential planar Hall effect (DPHE) (Mihajlović *et al.*, 2016), anisotropy

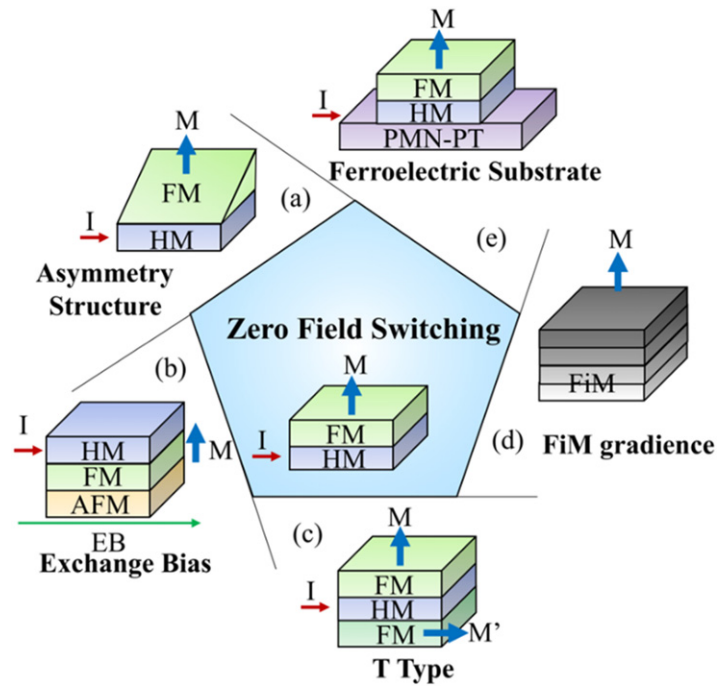


Fig. 5 Different approaches to reach zero-field switching. (a). Asymmetry structure, (b) Exchange bias system, (c) T-type structure, (d) Ferrimagnetic gradience stacking structure, (e) Ferroelectric substrate-based SOT structure.

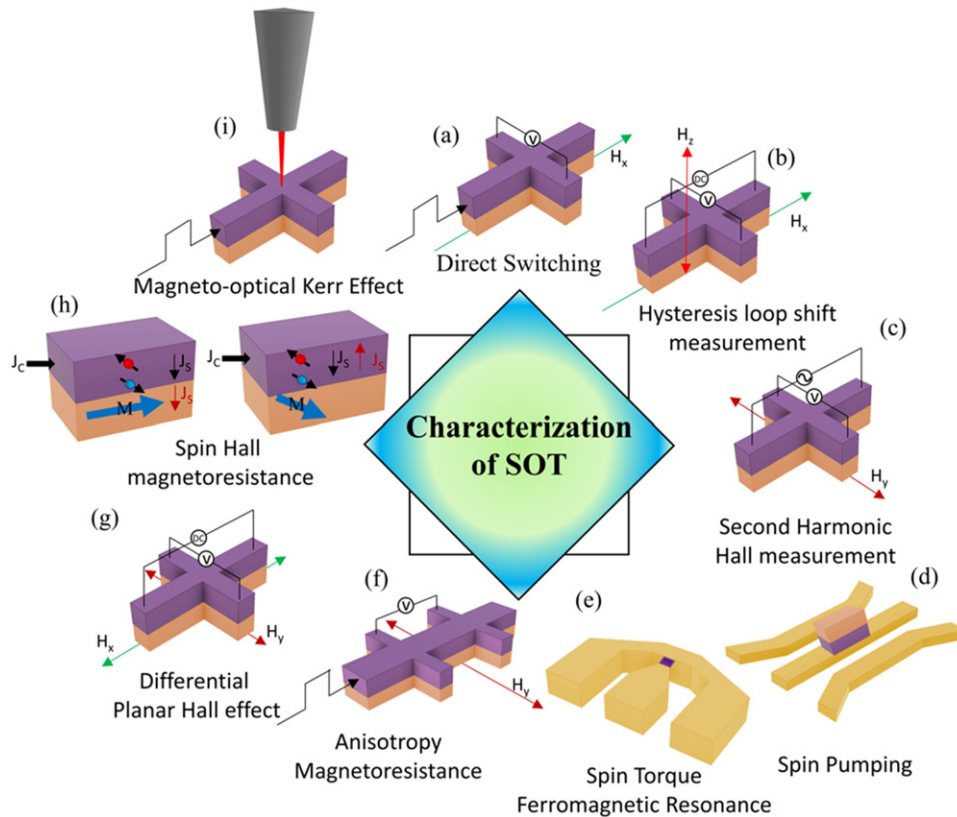


Fig. 6 Characterization techniques for SOT: (a) Direct switching, (b) Hysteresis loop shift measurement, (c) Second harmonic Hall measurement, (d) Spin pumping, (e) Spin torque ferromagnetic resonance, (f) Anisotropy magnetoresistance, (g) Differential planar Hall effect, (h) Spin Hall magnetoresistance, and (i) Magneto-optical Kerr effect.

magnetoresistance (AMR) measurements (Yang *et al.*, 2021), spin pumping, spin-torque ferromagnetic resonance (ST-FMR) (Liu *et al.*, 2011) and second harmonic Hall voltage measurements. Optical measurements such as magneto-optical Kerr effect (MOKE) are also included below.

Direct switching is done by passing a writing direct current (DC) pulse toward devices and it is closest to a practical MRAM writing process (Liu *et al.*, 2012b). By observing the switching behaviors, switching current density (J_{sw}) and H_{DL} can be extracted from the measurements. Generally, AHE data (field switching) are used to compare the direct switching data (SOT switching) to see the percentage of switching. The percentage of SOT switching usually accompanies with geometrical effects and other factors. Incomplete magnetization switching for SOT systems such as Pt/Co multilayers allows for multilevel switching, which is related to the relaxation of magnetic clusters (Huang *et al.*, 2017). Importantly, the SOT switching polarity depends on the sign of the SHA (Ghosh *et al.*, 2022; Liu *et al.*, 2020). In case of Pt (positive SHA) in the bottom layer, the polarity of a SOT switching curve is clockwise with positive H_x (along the current direction) (Yun *et al.*, 2017). In the rare-earth ferrimagnetic metals such as CoTb (Ueda *et al.*, 2017; Wu *et al.*, 2021), the magnetization is dominated by the transition metals above the compensation temperature. When the temperature is below the compensation point, the magnetization is dominated by the rare earth metal. For transport measurements such as AHE, magnetization direction associated with the 3d transition metal is followed. Therefore, the AHE polarity switches above/below the compensation temperature, and so does the SOT polarity (Ueda *et al.*, 2017; Wu *et al.*, 2021).

Hysteresis loop shift measurements were proposed by Pai *et al.* (2016). This technique simply measures AHE under a fixed extra bias magnetic field along charge current direction. When charge current passes by, it generates H_{DL} . Therefore, this effective field H_{DL} shifts the AHE loop. In other words, the AHE loop shifts to the opposite direction of the charge current direction. To clearly explain the mechanism, we need to take a step back and discuss the switching mechanism based on current-assisted domain wall (DW) motion. In the current-driven DW motion model, the current induced H_{DL} is more efficient to expand the Néel type DW rather than the Bloch type DW (Emori *et al.*, 2013). When the current passes through Néel type DWs, it generates an OOP effective field on the two sides of the DW with opposite directions ($\pm z$ directions), because spins at the two sides of DWs are opposite in the x -directions ($\rightarrow$ and $\leftarrow$). This means the two sides of the DWs move in the same directions. Therefore, there is no switching of magnetization. As the bias magnetic field is applied along the current direction (the x -axis), a large enough bias magnetic field (larger than the effective DMI field, H_{DMI}) can break the chirality of the DW, thus changing the spin orientation at the one side of the DW. The generated OOP effective fields now become parallel to each other. Hence, the two sides of the DW propagate or shrink and reach magnetization switching eventually. The loop shift measurement can not only yield H_{DL} but also $|H_{DMI}|$.

Second harmonic Hall measurements are simply characterized by an AC current source and a standard lock-in amplifier. The measurement assumes that the system behaves as a macrospin. Generally low frequencies (under a few kHz range) are chosen for the AC current source in order to make sure that the spins precess in-phase with the AC current. By applying an AC current towards a Hall cross device, the generated first ($V_{1\omega}$) and second harmonic ($V_{2\omega}$) Hall voltages are collected. Considering z -type SOT devices as an example (Kim *et al.*, 2012), $V_{1\omega}$ is analog to a DC current measurement which has a similar trend as a quadratic function when an applied external magnetic field is smaller than the effective anisotropy field (H_K). In other words, $V_{1\omega}$ measures how the magnetization responds to the external magnetic field. $V_{2\omega}$ describes how the AC current influences the magnetization with an applied magnetic field. Since charge current can generate spin current and transfer to STT, the generated STT should also fluctuate with the frequency of the AC current source. When the external magnetic field increases, the magnetization will tilt away from its easy axis, and the fluctuation generated by the AC current will also increase. Therefore, in case of PMA materials with negligible IP anisotropy, $V_{2\omega}$ will have a linear relationship with external magnetic field. The H_{DL} and H_{FL} are along the longitudinal (x -axis) and transverse (y -axis) directions with respect to the current directions, respectively. When an external bias magnetic field is applied along the x -axis or y -axis, we can obtain H_{DL} or H_{FL} . In typical conducting magnetic materials, the origin of Hall voltage is related to the AHE and the planar Hall effect (PHE). However, in systems that contain bilayers of magnetic insulators and heavy metals, the origin of Hall voltage comes from AHE-like and PHE-like spin Hall magnetoresistance (SMR) (Avci *et al.*, 2016; Li *et al.*, 2022). Although the second harmonic Hall measurement can give the magnitude of an effective field, its value needs extra corrections due to additional contributions from the spin Seebeck effect (SSE) and anomalous Nernst effect (ANE) (Avci *et al.*, 2016). Besides the z -type SOT devices, the x - and y -type SOT devices have also been characterized by second harmonic Hall measurements (Hayashi *et al.*, 2014).

Spin pumping is the only technique mentioned here that can measure SOT efficiency without any lithography process. Sample dimensions can be varied between micrometers and millimeters. The sample is placed underneath a coplanar waveguide (CW). Radio frequency (RF) is applied to the CW and the voltage of the sample is measured. The RF frequency excites spin precession in the FM layer and generates a spin current. Based on the inverse spin Hall effect (ISHE), the spin current flows inside the HM layer and converts into a charge voltage. The voltage signal comes from the mixture of ISHE and AMR. As a result, H_{DL} and α can be obtained from the spin pumping measurement.

Spin-torque ferromagnetic resonance was first proposed by Liu *et al.* (2011). It is widely used for detecting the SHA of metals and is different from spin pumping. A RF current is directly injected into the sample with STT and the voltage change is measured. In other words, ST-FMR is SOT-driven FMR, but spin pumping is the FMR driven ISHE. The measured voltage contains symmetric and asymmetric contributions, which means the collection of the amplitude of H_{DL} and Oersted field, respectively. As a result, H_{DL} , H_{FL} , and α can be extracted.

Differential planar Hall effect is related to the PHE voltage, which varies with the angle of magnetization (Mihajlović *et al.*, 2016). Let's consider R_{xy} again, with included polar (θ) and azimuthal (φ) angles. Hall voltages generally contain the AHE and the planar Hall effect (PHE). Assuming that current passes through the device along the x -direction, we can express the transverse resistance as $R_{xy} = \frac{1}{2}R_A \cos\theta + \frac{1}{2}R_P \sin^2\theta \sin 2\varphi$. Note that here we have ignored the contribution from OHE. When θ is 0 and 180° in

the z -type SOT structure, R_{xy} has clearly two distinguishable states. In the case of y -type devices, $\theta = 90^\circ$ and the stable states are at $\varphi \pm 90^\circ$. Hence, R_{xy} is not distinguishable. The concept of the DPHE is based on the bias magnetic field along the x -axis. The sequences of the measurement are: (1) apply a current pulse or change the magnitude of magnetic field along the y -direction. (2) When reading the resistance state, apply an extra magnetic field along two opposite x -directions and obtain the resistance difference. Hence, the switching current density and the corresponding switching field can be obtained.

Anisotropy magnetoresistance switching is the easiest and most direct way to yield SOT switching in IP systems compared to the DPHE, which needs to apply two external field directions. There are two main groups that proposed AMR for measuring IP materials. Yang *et al.* proposed SOT switching on y -type of materials (Yang *et al.*, 2021). In AMR measurements, an external magnetic field is applied along the y -axis. By comparing the AMR loop and the magnetic hysteresis loop, we can infer that the AMR peaks are analogous to multidomain states and low resistance states are single domain states. AMR switching is based on the virgin curve (zero to positive saturation magnetization field) measuring after current pulses are applied. If the pulse is large enough to change the magnetization direction, the virgin curve will first increase across to the multi-domain state, which is the AMR peak position, and then drop down to the minimum resistance state. Utilizing this method, we can directly define the switching current density of the system. In the same year, Liu *et al.* (2020) proposed a new concept of current-induced AMR loop shift. This concept is similar to the hysteresis loop shift measurement that has been employed in PMA systems. It comes from the SHE. SOT switching can also be achieved by sweeping the current pulse amplitude. In addition, the polarity of the SOT switching curve changes with sensing current direction which arises from the SHE-induced AMR loop shift. The upper and lower states of the magnetization change with changing sensing current directions. Therefore, H_{DL} , H_{FL} , and switching current density can be obtained.

Spin Hall magnetoresistance (SMR) originates from the SHE and ISHE that occur simultaneously. SMR is prominent in ferrimagnetic insulator (FMI)/HM bilayer systems compared to metallic systems. In this type of system, charge current fully passes through the HM layer. When the charge current induced spin polarization vector is non-collinear with respect to the magnetization of the FMI, spin current transmits to the FIM layer and the STT occurs. However, the spin current reflects back to the HM layer when the magnetization is parallel to the spin polarization vector. From SMR measurements, the magnitude of SHA can be extracted.

Magneto-optical Kerr effect (MOKE), an optical technique that can directly probe the reflected light polarization, also known as the Kerr rotation, and the Kerr rotation is proportional to the magnetization. Kerr effect refers to the magnetic response of a material through reflection, which is different from Faraday effect transmission-based measurements (Faraday, 1846). In other words, MOKE is sensitive to the surface and useful for various opaque substrates. Therefore, it is widely utilized as a surface magnetization probing technique. Based on the probing directional difference, it can be simply classified as polar (LL.D., 2009), longitudinal (LL.D., 2009), and transverse MOKE. Pump-probe (Ganguly *et al.*, 2014; Mondal *et al.*, 2017) (time-resolved MOKE) and Harmonic mode (Montazeri *et al.*, 2015) are the two methods to measure magnetization. Polar MOKE (PMOKE) is the most efficient method to probe z -type SOT devices (Lin *et al.*, 2019; Montazeri *et al.*, 2015; Tsai *et al.*, 2018). Through applying a current pulse, the magnetization dynamics can be probed by MOKE. For MOKE characterization, materials can be either patterned devices or sheet films, and geometrical problems for SOT switching can be eliminated in a single wire device (Lin *et al.*, 2019).

SOT Materials and Devices

Typical SOT devices contain two layers. The first layer, known as a spin current source, possess a strong spin orbit coupling to generate spin current. The earliest chosen spin current sources for SOT devices are simply HMs such as Pt (Woo *et al.*, 2014) and Ta (Jamali *et al.*, 2016), which are still the main materials for spin current sources. These two materials have strong spin orbit coupling and can be easily grown. On the other hand, spin orbit coupling (or spin Hall angle) can be improved by tuning the crystal orientation (Thompson *et al.*, 2021) and having proper crystal phase (Ghosh *et al.*, 2022). However, enhancing the spin Hall angle also gives rise to enhancement in electrical resistivity and hence the charge current shunting towards other layers. Therefore, besides the pure HMs mentioned above, HM-based alloys such as Pd-Pt (Zhu *et al.*, 2019) and W-Ta (Kim *et al.*, 2020) alloys have been proposed and shown to yield higher SHAs, with controllable electrical resistivity. Topological insulators (TI) have a bulk gap state but a gapless surface state (Fan *et al.*, 2022). The spin momentum locking in the surface state comes from the strong spin orbit coupling. This behavior is similar to the Rashba-Edelstein effect. When charge current passes through a TI layer, the Fermi surface shifts and generates spin accumulation. Two-dimensional (2D) materials have recently generated increasing attention, and many groups have studied 2D material-based SOT devices. Certain materials such as 2D transition metal dichalcogenides (TMDs) have strong spin orbit coupling and low crystal symmetry. TMDs such as WS_2 , $PtTe_2$, and WTe_2 are widely used for spin current sources (Xie *et al.*, 2021). Monolayer WTe_2 with extra mirror symmetry breaking, allows for extra out-of-plane spin polarization. As long as the charge current passes through the low symmetry direction, it can reach field-free switching when a PMA magnetic material is placed next to it. Some magnetic single layers (without extra spin current source) can also yield SOT switching, which is known as an anomalous SOT switching. The anomalous SOT is detectable in the transverse spin current when charge current is applied parallel to the magnetization direction (Wang *et al.*, 2019). Selective spin current sources are listed in Table 1.

Magnetic Layer for Magnetization Switching

Basic magnetic materials for SOT devices are FMs, and they are widely chosen as they have distinguishable two states. Among PMA FMs, ultra-thin Co, CoFeB, Co/Ni multilayers are often chosen for PMA SOT switching since they are more thermally stable. A

Table 1 Comparison of various SOT device properties: Power consumption $\sim r/(q_{SH})^2$; HM: heavy metal; AFM: antiferromagnet; 2DM: two-dimensional materials; Tis: topological insulators; PMA: perpendicular magnetic anisotropy; IP: in-plane magnetic anisotropy; DS: direct switching; ST-FMR: spin-torque ferromagnetic resonance; SHH: second harmonic Hall measurement; SP: spin pumping; MOKE: magneto-optic Kerr effect; RT: room temperature.

Spin current source	Stacking structure	Spin Hall angle (θ_{SH})	Resistivity of spin current source ($\mu\Omega$ cm)	Switching current density (A/cm^2)	Power consumption (10^{-5} Ω m)	Magnetic easy axis direction	Method	T (K)	References
HM	Pt/Co/AlO _x	0.08	23.5	2.3×10^7	3.67	PMA	DS	RT	(Liu <i>et al.</i> , 2012a)
	Pt/CoFe	0.085	28	–	3.88	IP	ST-FMR	RT	(Ganguly <i>et al.</i> , 2014)
	Pt/Py	0.056	20	–	6.38	IP	ST-FMR	RT	(Liu <i>et al.</i> , 2011)
	Pt/FGT	0.11	33.5	2.5×10^7	2.77	PMA	DS, SHH	180K	(Alghamdi <i>et al.</i> , 2019)
	Pt/CGT	0.25	150	–	2.4	PMA	SHH	5K	(Gupta <i>et al.</i> , 2020)
	β -W/CoFeB	-0.4	210	1.6×10^6	1.31	PMA	DS	RT	(Hao and Xiao, 2015)
	W/TmIG	-0.02	155	6×10^8	0.039	PMA	SMR, DS, SHH	RT	(Shao <i>et al.</i> , 2018)
	Ta/CGT	–	–	5×10^5	–	PMA	DS	4K	(Ostwal <i>et al.</i> , 2020)
	β -Ta/CoFeB	-0.12	190	–	13.2	PMA	ST-FMR	RT	(Liu <i>et al.</i> , 2012b)
	β -Ta/Py	-0.16	170	–	6.64	IP	ST-FMR	RT	(Tiwari <i>et al.</i> , 2017)
AFM	PtMn/Py	0.06	164	–	45.56	IP	SP	RT	(Zhang <i>et al.</i> , 2014)
	PdMn/Py	0.015	223	–	991.1	IP	SP	RT	(Zhang <i>et al.</i> , 2014)
	FeMn/Py	0.008	167.7	–	2620.3	IP	SP	RT	(Zhang <i>et al.</i> , 2014)
	IrMn/Py	0.022	269.3	–	556.4	IP	SP	RT	(Zhang <i>et al.</i> , 2014)
2DM	MoS ₂ /CoFeB	0.14	4760	–	242.9	IP	SHH	RT	(Shao <i>et al.</i> , 2016)
	MoTe ₂ /Py	0.032	556	–	543	IP	ST-FMR	RT	(Stiehl <i>et al.</i> , 2019)
	WTe ₂ /Py	0.013	380	–	26.4	IP	ST-FMR	RT	(MacNeill <i>et al.</i> , 2016)
	WTe ₂ /Py	0.09–0.51	580	2.96×10^5	2.23	IP	ST-FMR, MOKE	RT	(Shi <i>et al.</i> , 2019)
	WTe ₂ /FGT	4.6	444	3.9×10^6	0.021	OOP	DS	150K	(Shin <i>et al.</i> , 2022)
	NbSe ₂ /Py	0.005–0.013	167	–	988	IP	ST-FMR	RT	(Guimarães <i>et al.</i> , 2018)
	PtTe ₂ /Au/CoTb	0.05–0.15	33.3–333	3.1×10^5	13.32	OOP	DS, ST-FMR	RT	(Xu <i>et al.</i> , 2020)
	TaS ₂ /Py	0.25	16.7	5.1×10^5	0.267	IP	DS, ST-FMR	RT	(Husain <i>et al.</i> , 2020)
	(BiSb) ₂ Te ₃ /Mo/CoFeB	2.33–2.66	2500–5700	3×10^5	0.461–0.855	PMA	SHH, DS	RT	(Shao <i>et al.</i> , 2019)
	Bi ₂ Se ₃ /Py	0.3–1.75	1000–4117	6×10^5	1.34–11.1	IP	MOKE, ST-FMR	RT	(Wang <i>et al.</i> , 2017)
TIs	Bi _{0.9} Sb _{0.1} /Mn _{0.45} Ga _{0.55}	52	400	1.1×10^6	1.48×10^{-4}	PMA	DS	RT	(Khang <i>et al.</i> , 2018)
	Bi ₂ Te ₃ /FGT	0.7	–	2.2×10^6	–	PMA	DS	RT	(Wang <i>et al.</i> , 2021)

general requirement for PMA materials is to have sufficiently high H_K that retains the magnetization direction unchanged easily upon application of a bias magnetic field in the IP direction. In addition, too small H_K usually makes second Harmonic Hall measurements difficult. Magnetic materials should also exhibit good remanence (M_r) with clear two-states without magnetic field applied. Unlike z-type devices, IP SOT devices such as x-type and y-type have no significant requirements. The only thing that may influence materials choice is the requirement of specific x-type or y-type of switching. A magnetic material itself needs to have good magnetocrystalline anisotropy and shape anisotropy along a certain direction. Stray field becomes the main problem when shrinking down such SOT devices. In this context, FiMs with lower magnetic moments are the perfect class of materials in this context which can reduce stray fields effectively. AFM materials can be utilized as memristors that can work under high magnetic field environments since they are insensitive to low magnetic fields. By applying writing current pulses into certain AFM/HM bilayer structures, the Néel vector in the AFM can be rotated to control the system resistance. Wu *et al.*, 2022 proposed the FeRh Néel vector can be controlled by large pulse widths when FeRh is placed next to Ta. Joule heating induced from current pulse increases the FeRh temperature above the Néel temperature and changes the AFM to the FM state. Therefore, the generated spin current can exert torque on FeRh that changes the Néel vector when heat is dissipated.

Insulator-Based SOT Devices

Conventional SOT devices contain multiple metallic layers such as //Pt/Co which suffer from current shunting. Taking the advantage of insulating FiM, as well as utilizing the magnetic proximity effect and SMR, charge current can fully pass (100%) through a spin current layer without any current-shunting effect. The first FiM/HM SOT system was $\text{BaFe}_{12}\text{O}_{19}$ (BaM)/Pt bilayer proposed by Li *et al.* (2016). $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG), a well-known ultra-low damping material (Hauser *et al.*, 2016), and has been broadly studied for spin caloritronics (Uchida *et al.*, 2010). However, YIG generally has IP magnetic anisotropy, making the observation of magnetization switching rather challenging. Interestingly, Zhou *et al.* proposed to control sub-lattice magnetization direction based on the current pulse direction on an epitaxial YIG; a similar concept for controlling the Néel vector in AFM-based memristors (Bodnar *et al.*, 2018). Based on the pulse direction, the generated SOT simultaneously rotates the sub-lattice spin directions (clockwise or counterclockwise). As a result, the resistance exhibits two distinct states. On the other hand, YIG films grown on S-GGG, YSGG, GYSGG, and GSGG substrates have been reported to show PMA SOT switching, which arises from lattice mismatch (Guo *et al.*, 2019). Among different garnet systems, $\text{Tm}_3\text{Fe}_5\text{O}_{12}$ (TmIG) has gained lots of attention due to robust H_K and low compensation temperature (Quindeau *et al.*, 2016), which makes it a potential candidate for room temperature SOT device applications (Avci *et al.*, 2016). The DMI field was found in TmIG on $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ films, which was suggested to arise from the substrate oxide/oxide interface rather than the Pt/TmIG interface (Avci *et al.*, 2019). Spin Hall topological Hall effects (SH-THE) were observed when further reducing TmIG thickness with various capping layers such as Pt and W (Lee *et al.*, 2020). The observed SH-THE was claimed to be due to the interfacial DMI (Avci *et al.*, 2019). Such contradictory arguments might arise from the chosen substrate and the critical TmIG thickness.

In 2020, Caretta *et al.* have demonstrated that the interfacial DMI can be affected by growth substrate, heavy metal, and even the rare-earth orbital magnetism (Fig. 7) (Caretta *et al.*, 2020). Controlling the motion of skyrmions bubbles was also reported in the TmIG/Pt system based on skyrmions Hall effect (Vélez *et al.*, 2022). Considering SOT near compensation temperature, $\text{Tb}_3\text{Fe}_5\text{O}_{12}$ (TbIG) with compensation temperature (T_M) around 350K can reach the same polarity for SOT switching below/above the T_M owing to the joule heating effect that rises the device temperature above the T_M , which provides an interesting way for controlling polarity based on joule heating (Ren *et al.*, 2021). Another compensated FiM, $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ (GdIG), with T_M close to room temperature has also been studied (Li *et al.*, 2022; Liu *et al.*, 2021a,b).

2D Material-Based SOT Devices

2D material-based heterostructures have recently attracted a great deal of attention in the scientific community (Han *et al.*, 2021; Liu and Shao, 2020; Tang *et al.*, 2021). Weak Van der Waals (vdW) forces between layers allow for exfoliation of bulk (3D) crystals down to the monolayer (2D). Although graphene lacks strong intrinsic spin orbit coupling, it can be used to boost the PMA properties when interfaced with Co (Yang *et al.*, 2016). Certain 2D-vdW materials, especially transition metal dichalcogenides (TMDs), have strong spin orbit coupling and high spin Hall conductivity. Angstrom level surfaces allow generated spin currents to transfer to other layers without diphas. Low crystal symmetry yields new functionalities for applications. However, reducing the dimensionality of these vdW spin current sources may change the origin of spin current which is generally considered as SHE. This case especially happens in the monolayer limit. Therefore, low crystal symmetry plays a major role in the generation of extra spin current. In the case of TMDs, different types of spin torque can be generated based on the different structure asymmetries. The Dresselhaus effect refers to the generation of transverse spin current when charge current passes through the low symmetry crystal directions. In the case of WTe_2 , mirror symmetry is broken along the ac-plane (i.e., b -axis). As the charge current is applied through the b -axis, the spin current generated is transverse to the charge current direction. This allows extra OOP damping like torque, which indicates that an extra H_{DL} is generated along current direction. The effective field along the current direction allows for PMA SOT systems to reach small field or field-free SOT switching. Since 2D-vdW materials exhibit an ultra-flat interface, growth of non-vdW PMA magnetic materials on their surfaces is rather challenging. Therefore, most of 2D TMD-based SOT studies have focused on IP SOT devices, using ST-FMR and second harmonic Hall measurements. Taking the advantages of FiM with PMA properties, Xu *et al.* proposed a //PtTe₂/Au/CoTb structure with 2 nm Au to prevent the FiM from destroying the TMD interface during the deposition process, and direct switching was reached (Xu *et al.*, 2020).

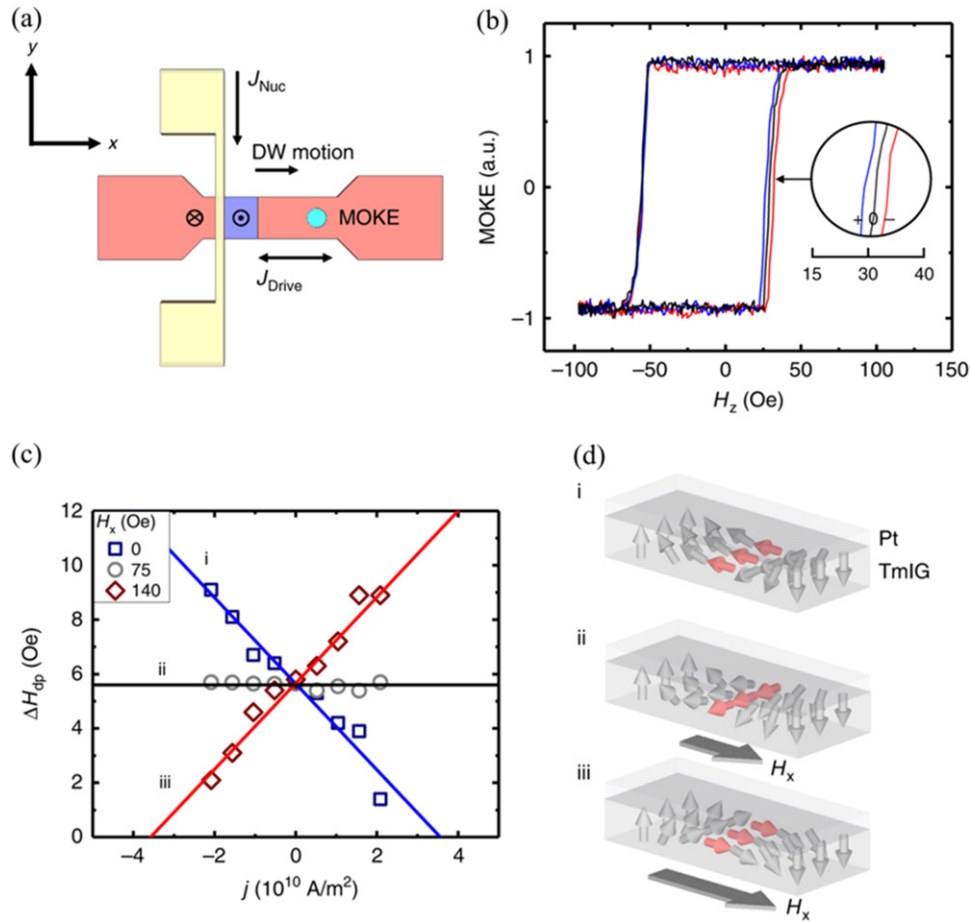


Fig. 7 Observations of domain wall motion in TmIG/Pt; (a) Schematic of the racetrack device for observing domain wall motion, (b) MOKE hysteresis loops and the loop shifts due to various sensing currents, (c) Propagation field as a function of current density under different bias magnetic fields, (d) Schematic of Néel type domain wall moments under bias magnetic fields. For further details, the readers are referred to Caretta, L., Rosenberg, E., Büttner, F., *et al.*, 2020. Interfacial Dzyaloshinskii-Moriya interaction arising from rare-earth orbital magnetism in insulating magnetic oxides. *Nature Communications* 11 (1), 1–9. Available at: <https://doi.org/10.1038/s41467-020-14924-7>.

Besides these 2D spin current sources, 2D vdW magnets such as Fe_3GeTe_2 (FGT) and CrI_3 have recently been explored. In particular, 2D FGT has been extensively studied owing to its high Curie temperature (T_C), close to room temperature, and strong PMA. SOT switching and second harmonic Hall measurements were performed on exfoliated FGT/Pt systems (Alghamdi *et al.*, 2019). Non-chiral skyrmions were also observed on FGT systems (Schmitt *et al.*, 2022). 2D CrI_3 exhibits AFM with “even” layer numbers (e.g., bilayer CrI_3) but FM with “odd” layer numbers (e.g., monolayer CrI_3). The AFM nature of bilayer CrI_3 arises from superexchange interactions between Cr atoms between the layers (McGuire *et al.*, 2015). Since the exchange interaction energy of the interlayer of CrI_3 is relatively weak, the AFM/FM state in 2D CrI_3 can be modulated by external stimuli. In case of the bilayer CrI_3 , it has been shown that gate-voltage (Huang *et al.*, 2018; Jiang *et al.*, 2018) and electron/hole doping (Jiang *et al.*, 2018) can control the magnetic state even with no applied magnetic field. Dolui *et al.* employed a $\text{TaSe}_2/\text{CrI}_3$ vdW heterostructure to switch the AFM to the FM state based on the SOT mechanism (Dolui *et al.*, 2020). On the other hand, utilizing low symmetry WTe_2 and FGT to form a WTe_2/FGT vdW heterostructure can also yield deterministic switching (Shin *et al.*, 2022). The main findings of this work are summarized in Fig. 8.

Since CrI_3 and FGT both have PMA properties, its CrI_3/FGT heterostructure with an electric field-controllable exchange bias effect/exchange anisotropy has also been proposed (Zhu *et al.*, 2020). Besides 2D materials acting as spin current sources or 2D magnets, MoS_2 has been used to enhance perpendicular magnetic anisotropy in the $\text{MoS}_2/\text{Pt}/[\text{Co}/\text{Ni}]_2$, which is attributed to the change in orbital hybridization (Xie *et al.*, 2019). While hBN is used as a protecting layer without spin orbit coupling, its orbital hybridization with the successive layer (SrRuO_3) induces Rashba spin orbit splitting and allows for SOT direct switching in the $\text{SrRuO}_3/\text{hBN}$ structure (Xie *et al.*, 2022). Although different 2D-3D/2D-2D heterostructures have been proposed, there are many unexplored interfacial phenomena, such as the magnetic proximity effect (Choi *et al.*, 2022). Robust spin torque efficiency and uniform quality are also required to build 2D SOT devices. In addition, most of the 2D heterostructures are created through mechanical exfoliation and/or chemical vapor deposition (CVD) which limit the scalability. Some have proposed a two-step growth process (sputtering and sulfuration/tellurization) or a direct sputtering to reach wafer scale. Achieving low power consumption and large-scale fabrication for 2D SOT heterostructures has remained a challenging task (Yang *et al.*, 2022).

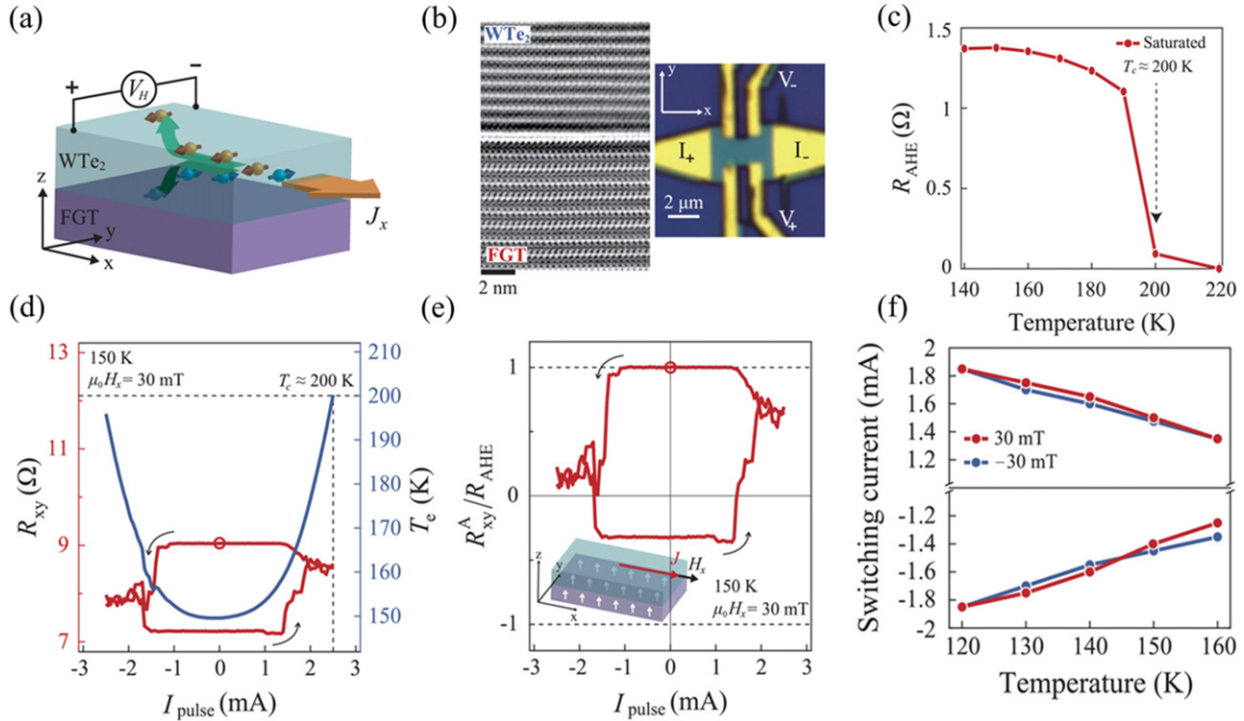


Fig. 8 (a) Stacking structure of the WTe₂/FGT device, (b) Cross-section scanning transmission electron microscopy image of WTe₂/FGT (left panel) and optical image of the Hall bar device (right panel); (c) Temperature dependence of anomalous Hall resistance; (d) Direct switching curve of WTe₂/FGT at 150 K with an applied H_x of 30 mT and the corresponding electron temperature during current pulse application; (e). Normalized SOT curve at 150 K; (f) Temperature dependent critical switching current under the positive/negative H_x . For further details, the readers are referred to Shin, I., Cho, W.J., An, E.S., *et al.*, 2022. Spin-orbit torque switching in an All-Van der Waals heterostructure. *Advanced Materials* 34 (8), 2101730. Available at: <https://doi.org/10.1002/ADMA.202101730>.

Concluding Remarks and Future Perspectives

It is very exciting to witness that STT-MRAM has recently joined the market. Instead of flash, Taiwan Semiconductor Manufacturing Company (TSMC) in collaboration with Ambiq successfully developed the 22 nm ultralow leakage process embedded STT-MRAM in 2020 (Yang *et al.*, 2022). Unlike STT-MRAM, SOT-MRAM needs a three-terminal structure to separate the writing and reading paths, so its structure is rather complex, with a large single bit volume, although the two-terminal structure was previously proposed using SOT and STT (Yu, 1928). Voltage control of magnetic anisotropy has recently been proposed for effectively switching bits with lower energy consumption (Nozaki *et al.*, 2019). In addition to MRAM applications, racetrack memory (Zhang *et al.*, 2016), spin logic devices (Liu *et al.*, 2011), neuromorphic computing (Zhou *et al.*, 2021), and spin torque diode oscillators have been proposed for SOT-based device applications. In its current SOT-MRAM, the critical switching current density lies in between 10^{10} and 10^{11} A m⁻², which is one order of magnitude higher than the complementary metal-oxide semiconductor (CMOS) part (10^9 A m⁻²) (Song *et al.*, 2021). The current MTJ and SOT-MRAM devices are mostly based on heavy metals, Pt and Ta, and CoFeB/MgO/CoFeB due to their high TMR and thermal stability. Although topological insulators can yield an extremely low critical switching current density, which is about 3 orders of magnitude smaller than that of CMOS components (Fan *et al.*, 2022), more work is needed to improve the stability and performance of the devices. The 2D material-based SOT technology has been rapidly expanding, but the large-scale controllable growth of uniform, air-stable 2D materials and device integration are in high demand (Yang *et al.*, 2022). The use of 2D materials in MRAM devices may pave the pathway to reduce the size of the bit and the critical current of SOT switching (reducing power consumption) while increasing the information storage density. The newly discovered vdW magnets have provided unprecedented opportunities for improving the performance of SOT-based devices. Further research is needed to realize this fully. It is anticipated that SOT-MRAM will become a competitive candidate and be available in the market in years to come.

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Antiferromagnets for Advanced Spintronics

Vijay S Kalappattil, Department of Physics, Colorado State University, Fort Collins, CO, United States

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Abstract

Antiferromagnets (AFMs) are magnetically ordered materials in such a way that the net magnetic moment is zero. For long since its original discovery in the 1930s, AFMs were thought of as interesting but useless materials. However, the last decade has witnessed a tremendous increase in AFM research owing to the discovery of anisotropic magnetoresistance (AMR), Spin-orbit Torque (SOT), Giant Anomalous Hall and Nernst effect (AHE and ANE), and many more, which are often considered to be a characteristic of ferromagnetic materials. Among many advantages an AFM offers, it intrinsically carries zero stray fields and possesses high spin precession frequency at Terahertz range, which have placed AFM spintronics on the map for futuristic technologies. In this article, we will review the current status of AFM research and its future perspectives.

Key Points

- AFM materials have zero stray fields and high spin precession frequency in terahertz range.
- AFM materials generate spin currents for spin caloritronic devices.
- Non-Collinear AFM such as Mn_3Sn can generate large AHE and ANE.
- Manipulation of spins in AFM can be achieved via electrical methods.
- SOT switching is achievable in AFM.

Introduction

Advantages of Antiferromagnetic Spintronics

Spintronics is a field of research where the spin degree of freedom of the charge carriers is manipulated to engender useful properties such as Giant magnetoresistance (GMR), Spin Hall effect (SHE), Anomalous Hall effect (AHE), etc. Traditionally spintronics relies on ferromagnetic material (FM) since it's easy to manipulate the spins in FM using a magnetic field or current. However, since the beginning of the last decade, antiferromagnetic materials (AFM) started attracting tremendous interest in the community due to the following reasons.

- (1) The magnetic ordering in AFM is unaffected by an external magnetic field.
- (2) In comparison to the up/down magnetic state in ferromagnets, AFM can host more than 2 states which could be utilized in neuromorphic/quantum computing technologies.
- (3) Long-range spin ordering in AFM is usually accompanied by net zero magnetization which leads to zero stray fields. Hence the storage density of AFM memory systems could be much higher than the current capabilities.
- (4) There is strong exchange interaction between AFM sublattices which leads to large exchange fields. As a result, spin precession in AFM occurs at the terahertz range, which is orders of magnitude higher than that of FM. This leads to the development of a new research field named Terahertz spintronics. In other words, the speed of magnetic state switching or writing using AFM is orders of magnitude higher than conventional spintronics systems.

In terms of spin ordering, one can loosely group antiferromagnets into two main categories: (1) collinear antiferromagnets with neighboring spins that are aligned antiparallel and (2) non-collinear antiferromagnetic (NCAFM) materials where the neighboring spins take on chiral formations of one sort or another and still yield a zero net magnetization. One example of NCAFM ordering is that three neighboring spins sit at the vertices of an equilateral triangle and point to the triangle center. The collinear antiferromagnets include transition metal monoxides such as FeO, NiO, CoO, and MnO, single-element antiferromagnets such as Cr and Mn, and Mn-based tetragonal alloys such as Mn_2Au and CuMnAs . As mentioned, the last decade has witnessed a huge interest in AFM research, and published work is abundant in the area. It would be impossible to mention everything in this article. Hence we limit the discussion to discoveries that are fundamentally important and hold great potential for futuristic technologies. For the benefit of our readers, especially newcomers to the field, we will first introduce some essential concepts of AFM physics.

Exchange Interaction

The primary origin of long-range order in a ferromagnetic material is the exchange interaction or spin-spin interaction. According to the Pauli-exclusion principle, two half-integer spin particles cannot occupy the same quantum state simultaneously. This leads to an antisymmetric total wave function when two electrons are exchanged. Now the variation between a singlet state ($S = 0$) and a triplet state ($S = 1$) results in an exchange constant or exchange integral,

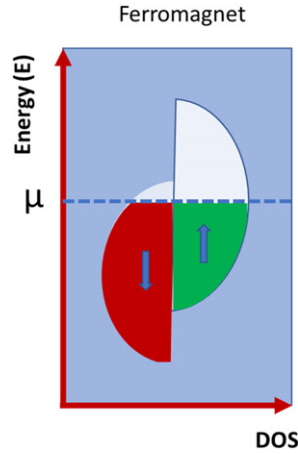


Fig. 1 Band structure for a spin-polarized material.

$$J = \frac{E_s - E_T}{2},$$

where E_s and E_T are the energies of the singlet and triplet states, respectively. The Heisenberg Hamiltonian for such a coupling can be written as

$$H = -\sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j.$$

Ferromagnetic or antiferromagnetic coupling in a solid is determined by the sign of J . Ferromagnetic coupling (or antiferromagnetic coupling), which is the parallel (or antiparallel) alignment of spins, occurs when $J > 0$ (or $J < 0$). Depending on the exact mechanism behind the exchange, it may be classified as a direct exchange, superexchange, RKKY interaction, or double exchange.

Spin-Orbit Interaction

The most important magnetic interaction in the context of this article is the spin-orbit interaction (SOI). The theory of SOI is derived from the relativistic theory when electron spin interacts with its motion. In a semi-classical picture, when an electron is orbiting around a nucleus in an atom, in the rest frame of the electron, the nucleus rotates around the electron. In that respect, the nucleus acts as a moving charge, thus producing a magnetic field B ,

$$B = \frac{E \times v}{c^2},$$

where v is the velocity of the nucleus and E is the radially-directed electric field generated at the position of the electron, with

$$E = -\frac{r}{r} \frac{dV(r)}{dr}.$$

Now the total spin-orbit Hamiltonian is given by the interaction of the magnetic field and electron spin,

$$H_{so} = \frac{e\hbar^2}{2m_e c^2 r} \frac{dV(r)}{dr} \cdot \mathbf{S} \cdot \mathbf{L},$$

where L is the orbital angular momentum and S is the spin angular momentum. Such an electromagnetic interaction directly results in the shift of an electron's atomic energy levels. Most of the spintronic phenomena such as anisotropic magnetoresistance (AMR), giant magnetoresistance (GMR), spin Hall effect (SHE), anomalous Hall effect (AHE), and anomalous Nernst effect (ANE) are a direct consequence of SOI.

Spin Current

The orbital motion of an electron around the nucleus gives rise to the orbital angular momentum. The orbital angular momentum can be quantified as

$$L = \sqrt{l(l+1)} \hbar,$$

where $\hbar$ is Planck's constant and l is the angular momentum quantum number. At the same time, the electron possesses an intrinsic angular momentum which gives rise to an intrinsic angular moment or spin. The spin quantum number, S , can take the value of $n/2$ where n is a non-negative integer. The flow of electrons, which constitutes electric or charge current, J_c , is the addition of both spin-up and spin-down electrons. In general, spin current, J_s , can be described as spin fluxes caused by electrical or thermal forces. Spin current is expressed as

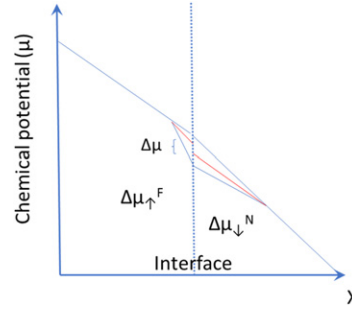


Fig. 2 Electrochemical potential difference for both spin-up and spin-down electrons.

$$S = \frac{\hbar}{2e} (J_{\uparrow} - J_{\downarrow}),$$

where $J_{\uparrow}$ and $J_{\downarrow}$ are the sum of up and down spin-charge current densities, respectively. In a broad sense, spin currents can be divided into different sections. When we have spin-up and spin-down electron imbalance within a material, this will result in a spin-polarized charge current (Boona *et al.*, 2014). In this case, J_s is accompanied by J_c . Spin-polarized current mainly occurs in ferromagnetic metals. Half-metallicity (conductor for spin up (or spin down) and insulator for a spin down (or spin up)) is observed primarily in ferromagnetic oxides and Heusler alloys. Fig. 1 shows a schematic representation of the energy levels for the spin-polarized band structure in a ferromagnetic metal.

μ in the figure represents the constant electrochemical potential at thermal equilibrium. However, μ may be different for spin-up and spin-down electrons, leading to two (separate) transport channels, (respectively) for both. Fig. 2 represents the spin diffusion across FM/NM interface derived from the continuity equation. By considering classical analogs of charge current, we can arrive at a continuity equation for spin angular momentum:

$$\frac{dM}{dt} = -\text{div } J_s,$$

where M is the total magnetization and J_s is the spin current density. This is analogous to the classical continuity equation $\frac{d\rho}{dt} = -\text{div } J_c$, where J_c is the charge current density and ρ is the charge density. But unlike charge, spin is not a conserved quantity. This would result in an additional term in the continuity equation:

$$\frac{dM}{dt} = -\text{div } J_s + T,$$

where T comes from the spin relaxation, which leads to non-conservation. Assuming the equilibrium condition, we can arrive at the spin diffusion equation,

$$\nabla^2 (\mu_{\uparrow} - \mu_{\downarrow}) = \frac{1}{\lambda^2} (\mu_{\uparrow} - \mu_{\downarrow}),$$

where the spin diffusion length $\lambda = \sqrt{D\tau}$. Here, D is the spin-averaged diffusion constant and τ is the spin-flip time.

Another type of spin current is “pure spin current”. In this case, the spin current is not accompanied by a charge current. Pure spin current can be thought of as an equal number of spin-up and spin-down electrons moving in the opposite direction. In that case, an effective angular momentum is transferred while the net charge transfer is zero. An alternative way of creating pure spin current is via magnons in a ferromagnetic insulator (Uchida *et al.*, 2010). Since magnons are quasiparticles that can transfer angular momentum by magnetic perturbation, in absence of conduction electrons, they are ideal for pure spin current experiments.

Spin Hall Effect and Inverse Spin Hall Effect

SHE is the phenomenon by which a flow of pure spin current is polarized perpendicularly to both the spin and charge current plane as an electric current is passing through the material with strong spin-orbit coupling. The Onsager reciprocity of SHE, which can convert spin current to charge current, is termed ISHE (Saitoh *et al.*, 2006). Although theoretically predicted in 1971 (Dyakonov and Perel, 1971), the first experimental observation was achieved in 2004 (Sinova *et al.*, 2004). Since then, SHE remains the fundamental pillar for spintronics research. SHE, in theory, is similar to the anomalous Hall effect (AHE), but the main difference is that SHE does not require broken time-reversal symmetry (magnetic field). The physical mechanisms behind AHE, SHE, and ISHE can be considered intrinsic or extrinsic depending on how external impurities are playing a role Fig. 3.

Intrinsic mechanism: In the case of a perfect crystal, the intrinsic contribution of spin Hall conductivity depends only on the spin-dependent band structure. In a simple picture, it originates from the Bloch wave function in momentum space (due to Berry curvature).

Extrinsic mechanism: The extrinsic contribution is mainly dominant in metals and semiconductors since this contribution depends on the excitation at the Fermi level. It can be further classified into the skew scattering and side jump mechanisms. In the first case, when a spin-carrying particle is scattered from impurities in the presence of strong SOI, the scattering cross section depends on the scattering angle and sign of spin and orbital angular momenta. Hence, depending on the state of the spin angular momentum, electrons will be

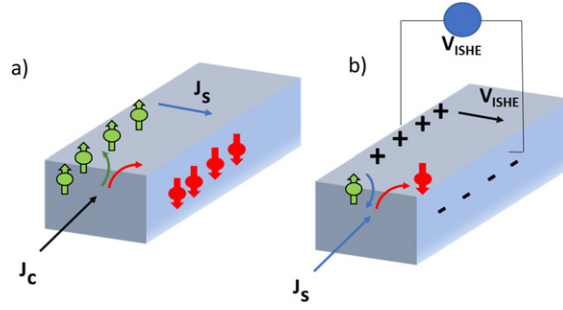


Fig. 3 Schematic representations of (a) Spin Hall effect and (b) Inverse Spin Hall effect in a strongly spin-orbit coupled metal.

scattered to the left or right, resulting in a potential. In the case of the side jump mechanism, where the scattering with impurities occurs again in the presence of strong spin-orbit coupling, it may result in a transverse shift of charge-carrying particles.

A term called spin Hall angle θ_{sh} is introduced to estimate the charge-to-spin conversion (or spin-to-charge) which occurs when a longitudinal charge current passes through the material. The spin Hall angle is defined as

$$\tan \theta_{sh} = \frac{\sigma_{sy}}{\sigma_{xx}},$$

where σ_{sy} is the spin Hall conductivity and σ_{xx} is the longitudinal charge conductivity. If ISHE for converting spin current to charge current, the converted charge current can be obtained using

$$J_c = \frac{\theta_{sh} 2e}{\hbar} J_s \times \sigma,$$

Collinear Antiferromagnet

Collinear Antiferromagnets are more of the traditional antiferromagnets. As the term indicates, here two sublattices are coupled with a spontaneous magnetic moment that is equal in magnitude and opposite in direction. If the temperature is increased, there exists a temperature called Néel temperature (T_N) above which the sublattices lose the spontaneous moment. Ever since the discovery of the AFM, it was thought of as a fundamentally interesting material with little to no use. Once Albert Fert and Peter Grunberg discovered giant magnetoresistance (GMR), it has led to a revolution in the data storage industry. In the GMR heads, AFM played a crucial role in pinning down the magnetic states in the adjacent ferromagnetic layers. This strong interface coupling or exchange bias effect started the beginning of AFM as materials with utility. However more and more theoretical works supporting spin manipulation in AFM began to come at the beginning of the last decade which eventually led to the surprising discoveries in AFM (Baltz *et al.*, 2018).

Detection of Anisotropic Magnetoresistance

The change in resistance, R when a magnetic field H is applied is known as magnetoresistance.

$$\frac{\Delta \rho}{\rho} = \frac{R(H) - R(0)}{R(0)},$$

Where $R(H)$ is the resistance at the field H and $R(0)$ is the resistance at the zero field. Since the discovery of magnetoresistance by Lord Kelvin in the 19th century, it has been exploited for a variety of magnetic sensors. In ferromagnetic materials, this magnetoresistance has a clear dependence on the relative directions of the magnetic field and electric current. This is termed anisotropic magnetoresistance (AMR). The origin of AMR is linked to spin-orbit interaction (SOI) and its effect on the s-d scattering of electrons. AMR is predominantly an effect seen in ferromagnetic materials. However it's being an even function of magnetic moment, one can expect it to arise in AFM as well.

One of the first experimental pieces of evidence came from a novel work by Park *et al.* (2011). They used a NiFe/IrMn(1.5 nm)/MgO/Pt tunnel junction device and observed $\sim 160\%$ tunneling anisotropic magnetic resistance (TAMR) at 4K, which was very much comparable to the values obtained from most ferromagnetic tunnel junctions. However, at higher temperatures above 100K, this value significantly decreases which limits its practical applications. Soon it was found that using [Pt/Co]/MnIr/AlO_x/Pt tunnel junctions, the antiferromagnetic moment in MnIr can be pinned along the easy direction of MnIr using in-plane fields due to the unidirectional anisotropy (Wang *et al.*, 2012). Due to the pinning effect, TAMR survives even at room temperature although values are much smaller compared to the previous work Fig. 4.

FeRh is a collinear antiferromagnet with uncommon magnetic transitions. This material is antiferromagnetic at room temperature and has an AFM to FM transition at ~ 400 K. The Curie temperature is at ~ 670 K. This uniqueness is used to demonstrate the pure AMR effect in AFM (Marti *et al.*, 2014). Here first the sample was heated above 400K (now in FM state) and applied a magnetic field sufficient enough to align the moment in the direction of the field. Then the sample was cooled to a low temperature (AFM state) in

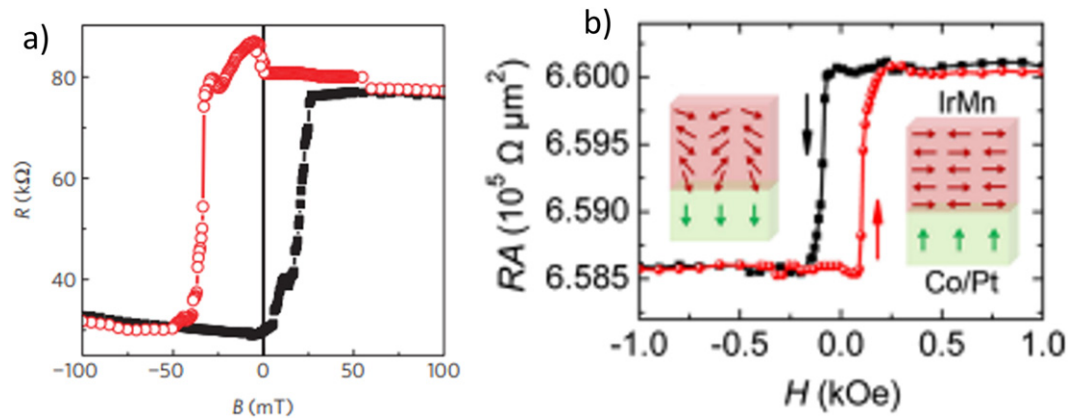


Fig. 4 (a) Magnetoresistance of the NiFe/IrMn(3 nm)/MgO/Pt tunnel-junction device (b) magnetoresistance when the field is perpendicular to [Pt/Co]/MnIr/AlO_x/Pt tunnel junctions. Taken from Park, B.G., Wunderlich, J., Martí, X., *et al.*, 2011. A spin-valve-like magnetoresistance of an antiferromagnet-based tunnel junction. *Nature Materials* 10 (5), 347–351. Available at: <https://doi.org/10.1038/nmat2983>. Wang, Y.Y., Song, C., Cui, B., *et al.*, 2012. Room-temperature perpendicular exchange coupling and tunneling anisotropic magnetoresistance in an antiferromagnet-based tunnel junction. *Physical Review Letters* 109 (13).

presence of that field (field cooled) and then removed the field. Then resistance was measured in the [100] crystal direction. They found that when the cooling field was applied along [100] or [010] direction, the resistance obtained was significantly different and reproducible under several successive measurements. This discovery could be a stepping stone for using AFM readout in memory devices. The same research group went on to show AFM AMR in La_{2/3}Sr_{1/3}MnO₃/Sr₂IrO₄ heterostructure as well (Fina *et al.*, 2014). Here Sr₂IrO₄ was used as the AFM element. What makes it further interesting is that Sr₂IrO₄ is an antiferromagnetic semiconductor. Mott gap opening in Sr₂IrO₄ due to the electron correlation and strong spin-orbit coupling introduced by Ir atoms makes this material a very interesting system for further explorations. Later many other AFM systems like semiconducting MnTe (Kriegner *et al.*, 2016), itinerant AFM EuTiO₃ (Ahadi *et al.*, 2019), Mn₂Au (Železný *et al.*, 2014), etc., also reported strong AMR effects.

Manipulation of AFM Spin via Current in Collinear AFM

Historically the main use of AFM materials was as the ferromagnetic pinning material in magnetic recording. For example, one of the first spin valve devices developed was based on NiFe/ Cu/NiFe/FeMn (Dieny *et al.*, 1991). Here The AFM FeMn is used to fix the magnetic moment in the adjacent NiFe layer so that we can easily write 1 s and 0 s using the changing moment in the other layer of NiFe. In modern MRAM devices which utilize tunneling magnetoresistance effect (TMR), strong interfacial exchange coupling from AFM such as MnIr, MnPt, etc., is used for fixing the reference layer. The reference layer here itself is another type of antiferromagnetic system called synthetic antiferromagnet (SAF). One method of writing using magnetic tunnel junctions is by only using an electric current. Here the property of spin current to transfer the angular momentum to the next layer is used to switch the free layer. This kind of torque generated is called spin transfer torque (STT). Although STT MRAM has its advantages and made tremendous improvements over previously existing technologies, it is not without problems or challenges. STT MRAM is not suited for very fast switching and also it's very much prone to the breakdown of the tunnel barriers as current is passing through all the layers. One possible option for overcoming that is using spin-orbit torque for switching. In a material with strong spin-orbit coupling, charge current can be converted to "pure" spin current via the spin Hall effect (SHE). In systems with broken inversion symmetry, Rashba- Edelstein effect can also create spin current density. This pure spin current can be used to switch the magnetic moment in the adjacent FM layer by domain wall motion. This kind of torque is spin-called spin-orbit torque (SOT). For more details about SOT switching in a ferromagnet, readers may refer to the article dedicated to SOT switching.

However, the torque generated here is not enough for fast switching most of the time. Hence as additional support, one has to apply a small in-plane magnetic field. But this will significantly reduce the dimensionality of the devices as it will affect the nearby ferromagnetic elements. One solution to this problem is to use exchange bias for providing an effective magnetic field. By using a simple FM/AFM interface we can easily achieve this. Different research groups have achieved this field-free switching by creating exchange-coupled IrMn (AFM)/FM layers (van den Brink *et al.*, 2016; Lau *et al.*, 2016; Fukami *et al.*, 2016; Oh *et al.*, 2016). By using SOT from AFM and assistance from EB, writing energy can be significantly reduced compared to the current technologies. This is one of the most promising directions for future MRAM devices Fig. 5.

Due to the peculiar spin structure, a new phenomenon called the magnetic spin Hall effect is discovered in NCAFM (Kimata *et al.*, 2019). More details about the effect are given in the next section. Similarly, an anomalous SHE is theoretically predicted in collinear AFM (Zhou *et al.*, 2020; Zhang *et al.*, 2021). This anomalous SHE could be originated from a combination of SHE and interaction between the spin Hall angle and magnetic field. One year later Chen *et al.* (2021) discovered an out-of-plane spin current in Mn₂Au which is now called as antiferromagnetic spin Hall effect. This gives the first experimental proof that collinear AFM can have intrinsic out-of-plane spin current and could be a huge boost in AFM data storage.

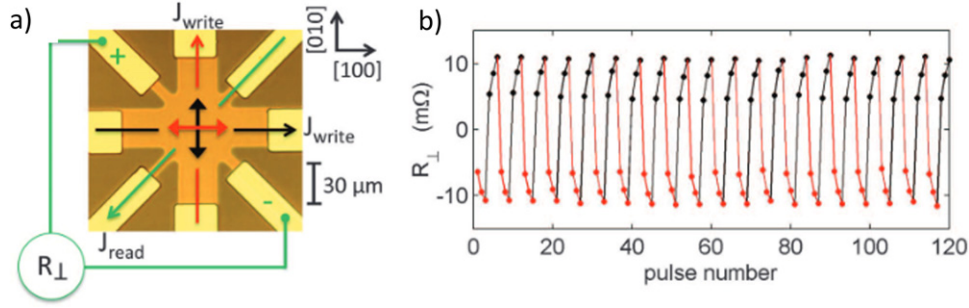


Fig. 5 (a) CuMnAs Device geometry for transport measurements (b) Change in transverse resistance measured. Measurement is done after passing 50 ms current pulses alternatively through [100] and [010] axis of CuMnAs. Taken from Wadley, P., Howells, B., Železný, J., *et al.*, 2016. Spintronics: Electrical switching of an antiferromagnet. *Science* 351 (6273), 587–590.

So far the discussion in this section has been about how to use collinear AFM for generating spin current or exchange bias that can be used to switch a ferromagnetic layer. However recent theoretical predictions and experimental discoveries have confirmed something which was unimaginable a few years back. Using antiferromagnet itself as a writing element by manipulating AFM spins. SOT effects have been shown to efficiently switch magnetic states in FM. At the same time, AFM also possesses SOT which can be utilized to switch AFM Neel order. In the first theoretical explanation for such a possibility, it was found that by using an AFM material in which two sublattices possess opposite local inversion symmetry and hence the opposite spin galvanic effect; we can achieve field-like torque in both sublattices due to the opposite spin accumulation (Železný *et al.*, 2014). Although the first theoretical prediction was on Mn₂Au, a couple of years later it was experimentally demonstrated in CuMnSn (Wadley *et al.*, 2016). CuMnSn has a similar crystal structure to that of Mn₂Au. Wadley *et al.* showed that by injecting a charge current, they could switch the Neel order by 90 degrees. By using the AMR technique they were able to detect the rotation of Mn moment perpendicular to the current direction. Later it has been shown that two orders of magnitude higher switching speed compared to typical FM can be achieved in CuMnSn (Olejník *et al.*, 2018). Furthermore, other AFM materials with similar structures have been shown to switch with better thermal stability (Bodnar *et al.*, 2018; Zhou *et al.*, 2018).

AMR and planar Hall effect (PHE) has been the main detection technique used in this system. Logically, the next question would be whether it is possible to rotate the spins using torque generated by passing a current through adjacent heavy metals like Platinum similar to what is expected for a ferromagnet. In general, SOT is composed of 2 parts. Field-like torque and a damping-like torque. When used with PMA material, damping-like torque assists the switching while field-like torque rotates the magnetization towards the in-plane direction. When a similar concept is applied in the case of rotating a Neel vector in AFM, the exchange torque generated between two sublattices gets compensated by the field-like torque. Hence this torque will not be assisting much in spin rotation. On the other hand, damping like toque could generate enough canting in the magnetic moment and help rotate the Neel vector. However, detecting this switching with complete scientific consensus has been challenging. The main reason is because of the detection technique. Signals detected using AMR or SMR technique could be contaminated by thermal or electrical components, especially the higher current density used in this experiment. Chiang *et al.* (2019) argued from the measuring planar Hall signal that in Pt/NiO/glass and Pt/glass structures, there is no evidence for Neel vector rotation. This raises the need for convincingly measuring AFM switching. Finally, in 2020, Cheng *et al.* measured Neel vector switching in Pt/ α -Fe₂O₃ bilayers through AHE. They observed 2 different types of signals from as-grown samples and annealed samples. A proper step-like signal was observed in the annealed sample indicating SOT switching, while saw tooth-type signals from as-grown samples are artifacts coming from Pt (Cheng *et al.*, 2020).

Thermal Generation of Spin Current in AFM

In the field of spintronics, the spin degree of freedom in the charge carriers is manipulated in to be utilized in achieving various interesting properties. One way of controlling this spin degree of freedom is by using a temperature gradient. There is a subfield of spintronics dedicated to controlling spin and heat coupling called spin caloritronics. The area of spin caloritronics gained momentum when Uchida *et al.* (2008) discovered the spin Seebeck effect (SSE) in a FM metal. When a temperature gradient ∇T is created between a ferromagnetic material, F, and a non-magnetic material, NM, a flow of spin current is generated and is injected from F to NM. If the spin-orbit coupling in NM is good, the injected spin current is converted into a detectable voltage, via ISHE. Since then SSE has been observed in insulators and semiconductors as well. The spin current generated can be defined as

$$I_s \approx \frac{\gamma \hbar G_r k_b}{2\pi M_s V} (T_m - T_N),$$

where $\frac{\gamma \hbar G_r k_b}{2\pi M_s V}$ is called the interfacial coefficient, L_s . This implies that the magnitude of SSE is mainly correlated to the temperature difference between magnons in FM and electrons in NM and the spin mixing conductance at the interface. Now in the NM layer, a voltage is generated from this I_s using ISHE as explained in the previous section,

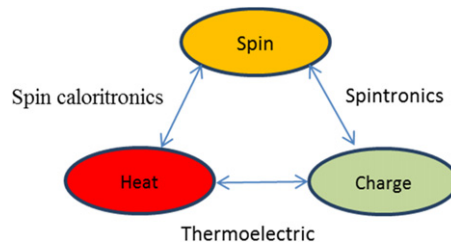


Fig. 6 Schematic representing coupling between spin caloritronics, thermoelectrics, and spintronics.

$$V_{ISHE} = \frac{\theta_{SHE} I_s \rho}{w},$$

where ρ the electrical resistivity and w is the width of a platinum strip. **Fig. 6.**

The majority of the research in SSE has been done on ferromagnetic insulators. Given that most of the magnetic insulators are antiferromagnetic, it raises the question of the thermal generation of spin current in AFM and the possibility of momentum transfer through antiferromagnetic spin waves. [Seki et al. \(2015\)](#) obtained the first result in this direction in 2015 in single crystal $\text{Cr}_2\text{O}_3/\text{Pt}$ bilayers. Upon application of thermal gradient across the layers, a voltage has been detected on Pt using ISHE. This voltage was proportional to the magnetization in Cr_2O_3 which confirms the role of AFM spin waves as a spin current carrier. Even the spin-flop transition in magnetization is visible in the ISHE data. Later [Wu et al. \(2016\)](#) showed the effect is prevalent in another AFM MnF_2 as well. MnF_2 capped with Pt showed the SSE, which is significantly higher than that of YIG - the most common material studied for the thermal generation of spin current.

Another important role of AFM in thermal spin transport is to tune the spin mixing conductance at the interface. As given in the above equation spin mixing conductance directly influences the magnitude of SSE voltage. When antiferromagnetic insulators like NiO or CoO are inserted between YIG and Pt, SSE magnitude improved more than 10 times. They attributed this drastic increase to the magnons and spin fluctuation in the thin AFM layer ([Lin et al., 2016](#)).

Spin Pumping in AFM

Like in the previous session, another way of generating pure spin current is through spin pumping. Typically, spin pumping refers to the generation of pure spin current (J_s) via coherent magnetization precession in FM/metal systems. When the ferromagnetic resonance conditions are fulfilled by a driven applied microwave field, a part of the angular momenta is pumped into the metal adjacent to it due to the s-d exchange coupling ([Tserkovnyak et al., 2002](#)). If the metal has good SOC, this angular momentum or spin current can be detected using the inverse spin Hall effect (ISHE). The most studied material for spin pumping is YIG and NiFe due to their low damping, high Curie temperature, and low anisotropy. In the case of FM, the spin precession frequency is in the range of GHz. However, when it comes to AFM, spin precession depends on magnetic anisotropy and exchange fields. Due to the higher exchange field in AFM, the spin precession in most AFM reaches the terahertz regime. This led to the development of Terahertz spintronics. Two of the most important discoveries came in 2020. Firstly, [Li et al. \(2020\)](#) reported spin pumping in the terahertz regime in a uniaxial antiferromagnet $\text{Cr}_2\text{O}_3/\text{HM}$ system. They reported two distinct resonances while sweeping the magnetic field. At a resonance field of 2.7 Tesla, antiferromagnetic resonance is at 0.24 THz frequency. Another resonance is obtained at 10.5 T due to the spin canting. Both of these resonances generate pure spin current as is evident from sign flipping when the heavy metal change from Pt to Ta. Temperature dependence measurements prove that both coherent and incoherent magnons contribute to the spin current with incongruent magnons dominating at low temperatures. At the same time, [Vaidya et al. \(2020\)](#) found sub-THz resonance in MnF_2 . Antiferromagnetic resonance field in MnF_2 is found to be 0.25 THz. Further control experiment hints toward coherent spin pumping in this material. Since then many groups have successfully tried to achieve AFM resonance in a variety of AFM materials. A couple of examples include NiO ([Moriyama et al., 2020](#)) and $\alpha\text{-Fe}_2\text{O}_3$ ([Boventer et al., 2021](#); [Wang et al., 2021](#)).

Non-Collinear Antiferromagnetism

So far we discussed traditional collinear AFMs in which sublattice moments align as opposed to each other and produce net zero moments. Another possibility of achieving zero net magnetization is by arranging the neighboring spins to form a chiral structure and canceling the net moment. An example of such an arrangement is given in **Fig. 7**. In Mn_3Sn , the Mn ions are magnetic, with a magnetic moment of $\sim 3 \mu_B$ per Mn ion, while the Sn ions are non-magnetic. If one considers a triangle consisting of three Mn ions on the vertices, the spins of the Mn ions form a triangular structure, with two pointing along the triangle edges and the third pointing to Sn. This spin triangle has a vector chirality opposed to the usual 120-degree structure and is therefore often referred to as an inverse triangular spin structure. Thus, Mn_3Sn is mostly an easy-plane antiferromagnet, which is in the c plane in the easy plane, there is a local easy axis that points from Mn to its neighboring Sn. When one spin points along the easy axis, the other two spins tilt slightly towards the easy axis; this results in very weak magnetization, $0.002 \mu_B$ per Mn ion. Such spin ordering results from the combination of (1) Heisenberg exchange and (2) Dzyaloshinskii-Moriya interaction between the Mn ions and (3)

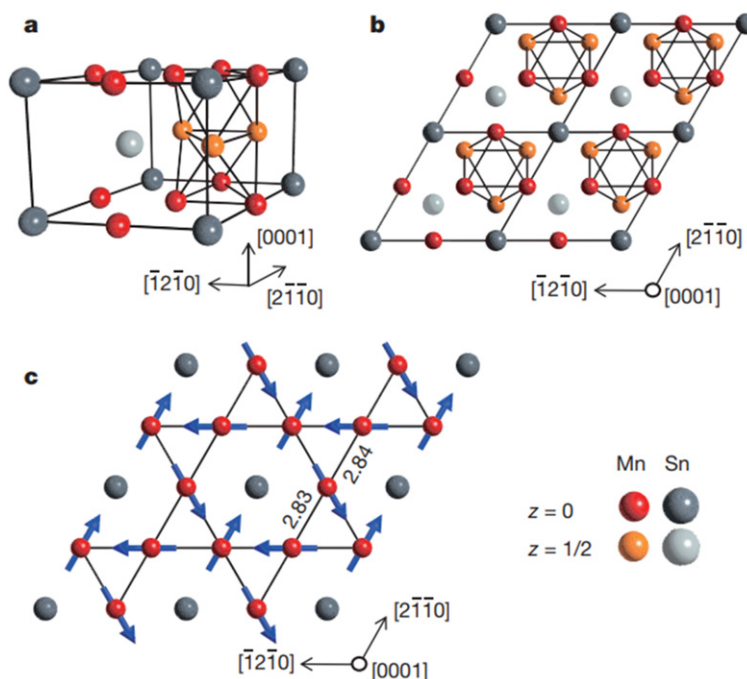


Fig. 7 (a) Crystallographic unit cell of Mn_3Sn (b) Top view along the c axis of the neighboring four unit cells in the a - b plane. Taken from Nakatsuji, S., Kiyohara, N., Higo, T., 2015. Large anomalous Hall effect in a non-collinear antiferromagnet at room temperature. *Nature* 527 (7577), 212–215.

single-ion anisotropy associated with Sn ions, with (1) being the strongest and (3) being the weakest. This AFM ordering is present in Mn_3Sn over 50–420K, where 420K is the Neel temperature. Below 50K, Mn_3Sn is ferromagnetic due to the canting of spins along the c -axis. Now we will look at the tremendous progress made in the area of NCAFM in the last few years.

Anomalous Hall Effect (AHE) and Anomalous Nernst effect (ANE)

For more than a century, it's known that ferromagnetic materials exhibit an anomalous Hall effect (AHE); the generation of a transverse voltage (V_{xy}) when a current is applied even in the absence of a magnetic field (Nagaosa *et al.*, 2010). Although plenty of experimental evidence for AHE has been achieved over the years, theoretical consensus was lacking until recently. Now we know that AHE has both intrinsic and extrinsic contributions that depend mostly on scattering and intrinsic mechanisms that are independent of scattering. This extrinsic contribution has been explained using the momentum space geometrical effects or Berry phase (Sundaram and Niu, 1999). This AHE increases linearly with an applied magnetic field. However, in a novel theoretical work in 2014, Chen *et al.* (2014) predicted that in Mn_3Ir , a noncollinear AFM can have large AHE even in the absence of spontaneous magnetization. The unit cell of Mn_3Ir forms a triangular atomic order with Mn forming a Kagome lattice. Mn_3Ir does not have (111) mirror symmetry due to this arrangement. Due to this, large SOC in the Ir atom will be transferred to Mn atoms which stabilizes a large AHE in the material. This AHE is also dependent on the crystallographic direction.

In the following year, Nakatsuji *et al.* (2015) confirmed this experiment in bulk single crystal Mn_3Sn . An Anomalous Hall conductivity value of $\sim 20 \Omega^{-1}/\text{cm}$ was obtained at room temperature. This large value cannot be explained by the extremely small magnetic moment of $\sim 0.002 \mu_B$ originating from slight canting. This further proves the AHE originating from the enhanced Berry curvature in Mn_3Sn . Following the discovery in Mn_3Sn , several NCAFMs have been reported to exhibit giant AHE such as Mn_3Ge (Kiyohara *et al.*, 2016), Mn_3Pt (Zhao *et al.*, 2022), Mn_3AN ($A = \text{Ni, Cu, Zn, Ga, Ge, Pd, In, Sn, Ir, Pt}$) (Huyen *et al.*, 2019), Mn_3Ir (Iwaki *et al.*, 2020), etc.

Since the Anomalous Nernst effect (ANE) is the thermal counterpart of AHE, theoretical predictions were performed in 2017 about the giant Anomalous Nernst effect in Mn_3Sn . From the relativistic *ab initio* calculations, Guo *et al.* showed the ANE conductivity in Mn_3Sn is an order of magnitude higher than typical Ferromagnet such as Iron (Guo and Wang, 2017). In 2017 Li *et al.* (2017) also predicted the giant ANE in Mn_3NS and confirmed that it has a pure topological origin. Soon Nakatsuji's group showed the giant ANE in single crystals of Mn_3Sn (Ikhlas *et al.*, 2017). They obtained a transverse Seebeck coefficient of $\sim 0.35 \mu\text{V/K}$ at room temperature. They also found that the values varied significantly with slight changes Mn_3Sn chemical composition. This is due to the fact that with different Mn concentrations, the Fermi level (E_F) moves relative to the Weyl points. Guo *et al.* also predicted a spin Nernst value similar to that of Pt from Mn_3Sn . This is yet to be shown experimentally and remains an open subject for future research (Guo and Wang, 2017).

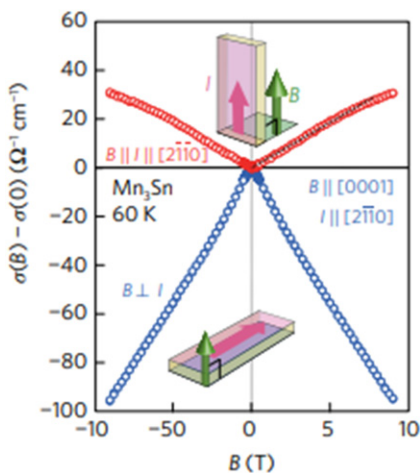


Fig. 8 Magnetic field dependence of magnetoconductivity in Mn_3Sn single crystals. Taken from Kuroda, K., Tomita, T., Suzuki, M.T., *et al.*, 2017. Evidence for magnetic Weyl fermions in a correlated metal. *Nature Materials* 16 (11), 1090–1095. Available at: <https://doi.org/10.1038/nmat4987>.

Evidence of Weyl Fermions and Chiral Anomaly in Mn_3Sn

Another fundamentally important discovery in NCAFM is the observation of Weyl Fermions in Mn_3Sn . Weyl Fermions are massless particles with half-integer spins. Until recently, Weyl fermions were not observed experimentally in nature although theoretical predictions were made long back in quantum field theory (Xu *et al.*, 2015). Crystalline solids that can host Weyl Fermions are called Weyl semimetals and they possess a characteristic Fermi arc in their electronic structure. These Fermi arcs connect the Weyl points of opposite chirality. One necessary criterion for a crystalline solid to be Weyl semimetal is it should either break time-reversal symmetry (TRS) or inversion symmetry (or both). When one of the symmetries is broken, two nondegenerate energy bands can linearly touch at pairs of isolated points in momentum space (Weyl nodes). Here TRS breaking systems are particularly interesting due to the coupling between magnetism and electron correlations. Ever since the first discovery of Weyl semimetal TaAs (Xu *et al.*, 2015), different groups have identified many complex compounds that can host Weyl Fermions. In 2017, Kuroda *et al.* extended the search for Weyl Fermion hosting materials to NCAFM. Through a combination of Angle-resolved photoemission spectroscopy (ARPES), anomalous Hall measurements, positive longitudinal conductance, and negative transverse magnetoconductance measurements, they concluded that Mn_3Sn is indeed a Weyl semimetal (Kuroda *et al.*, 2017).

In TRS-breaking systems that host Weyl fermion, one important feature emerges in transport measurements, negative magnetoresistance. This is indeed one of the indirect measurements for the chiral anomaly. In presence of the magnetic field, Dirac cones will split into two with one supporting left-handed and the other supporting right-handed Fermions. At this point, the system has a chiral symmetry. However, upon application of an electric current parallel to the magnetic field, this chiral symmetry may break, and charge carriers will flow from one Weyl node to another. This will result in an effective negative magnetoresistance (NMR). In the case of Mn_3Sn , due to the scattering between Weyl points, positive longitudinal magnetoconductance is observed. But strong negative transverse magnetoconductance indicates the presence of Weyl Fermions as shown in Fig. 8. However, one has to be very careful in characterizing chiral anomaly just by the observation of NMR. There are some semimetals where NMR is reported with having a Dirac dispersion (Tsidilkovskii *et al.*, 1974; Breunig *et al.*, 2017). Unfortunately, strongly correlated effects in Mn_3Sn prevent observing clear Fermi Arc from ARPES. Hence more detailed studies are needed to reach a complete consensus on Weyl physics in Mn_3Sn .

Spin Current and Magnetic Spin Hall Effect (MSHE)

Following the discovery of the giant AHE in the Mn_3Sn , a lot of attention has been given to the possibility of using this effect for controlling the spin and developing potential applications. Zeleny *et al.* found that the spin-polarized current in this Mn_3X AFM is in a similar order of magnitude to that of conventional ferromagnets. This is particularly dramatic given the absence of strong spin-orbit coupling (Železný *et al.*, 2017). This obtained spin current is also the result of symmetry breaking arising from the triangular magnetic structure. They also showed that it is possible to have both longitudinal and transverse spin currents at the same time. The longitudinal spin current is analogous to the spin-polarized current in ferromagnets while the transverse one is analogous to the spin current generated by (SHE). However, it is important to note that this transverse current is odd under time-reversal symmetry while that generated by SHE is even. Another important point to mention about Mn_3Sn is the facet-dependent spin Hall effect (Zhang *et al.*, 2016). The magnetization of Mn is arranged triangularly in the (111) plane. Hence less symmetry directions such as (001) exhibit larger SHE compared to (111). Zhang *et al.* reported a value of spin Hall angle as ~ 0.35 in the (001) direction, which is higher than what is found in most heavy metals. Later Zhou *et al.* (2020) reported an even higher value of 1.01 in Mn_3Ir .

Table 1 List of a few important AFMs and their ordering temperatures (T_N)

Material	Néel temperature (T_N)	Important works
NiO	~525K	Moriyama <i>et al.</i> (2020)
Mn ₃ Sn	~420K	Nakatsuji <i>et al.</i> (2015)
Mn ₃ Ge	~380K	Nakatsuji <i>et al.</i> (2015)
MnF ₂	~67K	Wu <i>et al.</i> (2016)
α -Fe ₂ O ₃	~966K	Boventer <i>et al.</i> (2021)
Cr ₂ O ₃	~307K	Seki <i>et al.</i> (2015)
CuMnAs	~350K	Wadley <i>et al.</i> (2016)
FeMn	~483K	Dieny <i>et al.</i> (1991)
Mn ₂ Au	~1575K	Železný <i>et al.</i> (2014)
EuTiO ₃	~5.5K	Ahadi <i>et al.</i> (2019)
Sr ₂ IrO ₄	~240K	Fina <i>et al.</i> (2014)
MnTe	~323K	Kriegner <i>et al.</i> (2016)
FeRh	~400K	Marti <i>et al.</i> (2014)
MnIr	~1145K	Park <i>et al.</i> (2011)
CrI ₃	~45K	Huang <i>et al.</i> (2018)
CrCl ₃	~17K	McGuire <i>et al.</i> (2017)
BiFeO ₃	~653K	Martin <i>et al.</i> (2008)

The above-mentioned time reversal (T) odd spin current potentially causes newly discovered magnetics spin Hall effect (MSHE). It can be understood as a result of the redistribution of electrons with certain spin orientations at the Fermi level in response to an external electric field. In terms of the charge current-to-spin current conversion efficiency, the effective spin Hall angle θ_{SH} is predicted to be $\sim 15\%$, much larger than values compared to those of commonly used heavy metals. For the normal spin Hall effect in Mn₃Sn, any spin current in the thickness direction will also contain an in-plane spin component. However, this component will be relatively small as the normal spin Hall response in Mn₃Sn is an order of magnitude weaker than the MSHE response. Mook *et al.* (2020) explained this using constant relaxation approximation that this MSHE in Mn₃Sn arises due to the spin current vortices in the Fermi sea. This explanation is also true for MSHE and a yet-to-be experimentally confirmed effect, the magnetic spin Nernst effect (MSHE).

Manipulation Spin via Current in Non-Collinear AFM

As mentioned in the above section, NCAFM is a source for the exciting new spin current generation. Now the obvious question would be if one can manipulate the AFM spins in these systems similar to the mentioned ones in collinear AFM. NCAFM can also be used as a source for providing an exchange coupling and hence pinning down the magnetic state in FM layers. This enhances the possible selection of materials available for current EB-based technologies. Due to the inherent triangular structure, NCAFM possesses low symmetries which can result in the generation of out-of-plane torque. In 2020, Zhou *et al.* (2020) found an anomalous out-of-plane torque in Mn₃Ir. Due to the fact that Mn₃Ir has a face-centered cubic lattice and triangular spin structure, it possesses 3 fold rotational symmetry along the [111] axis. Other axes in the material do not possess complete symmetries. Hence if one passes current through a low symmetry axis, that would result in an out-of-plane torque. Zhou *et al.* (2020) have detected this torque by means of spin torque FMR. Similarly, the out-of-plane torque has been detected in Mn₃GaN as well (Nan *et al.*, 2020). In the previous session, we mentioned spin current generated in the out-of-plane generation (MSHE). This out-of-plane current can be utilized for field-free switching of magnetization in perpendicular magnetic anisotropy (PMA) materials. This has been experimentally observed by You *et al.* (2021) using antiperovskite antiferromagnet Mn₃SnN. They prepared a multilayer structure consisting of Mn₃SnN/[Co/Pd]₃. Here Co/Pd multilayers act as the PMA material. The anomalous Hall effect is used for detecting magnetic switching in this work. A similar result was reported for Mn₃Sn/[Ni/Co]n structure as well (Hu *et al.*, 2022).

Detecting the magnetization switching is complicated in collinear AFM. However, when it comes to NCAFM, thanks to its large AHE, the detection of switching using AHE is fairly easy. Also, Higo *et al.* (2018) reported a large magneto-optic curve effect in Mn₃Sn which can also be used for detection purposes in laboratories. The first experiment demonstrating the AHE switching in noncollinear AFM is reported in 2020 by Tsai *et al.* (2020). They used a similar methodology used in FM switching. A multilayer stack of polycrystalline Mn₃Sn and heavy metal is grown using magnetron sputtering. A current density in the range of 10^{11} A is used to switch the AHE signal. Interesting the Hall signal polarity is determined by the spin Hall angle of the metal used. (positive for Pt, almost zero for Cu, and negative for W). Takeuchi *et al.* (2021) showed that in Mn₃Sn/heavy metal structure upon application of an electric current, the hall resistance fluctuates due to the rotation of the chiral spin structures of Mn₃Sn. These two experiments provide an exciting new avenue for future memory elements.

For the benefit of our readers, Table 1 lists some of the most important antiferromagnetic materials and their ordering temperatures.

Conclusion and Future Perspective

AFM spintronics has been expanding at a rapid pace in recent years owing to the discoveries of new materials and outstanding properties. After being played an assisting role in spintronic devices for three decades, antiferromagnetic materials are finding their own way to mainstream research and devices. Although highly promising results have been obtained from collinear and non-collinear AFM, the development of AFM-based devices for practical use is still in its infancy. But due to its significant advantages over FM spintronics, AFM spintronics is expected to play a critical role in future computing technologies such as Neuromorphic computing and quantum computing.

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Multifunctional Magnetic Oxides: Neutron Diffraction Studies

Denis P Kozlenko, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia

The-Long Phan, Faculty of Engineering Physics and Nanotechnology, VNU-University of Engineering and Technology, Hanoi, Vietnam

Manh-Huong Phan, Department of Physics, University of South Florida, Tampa, FL, United States

Ngoc-Toan Dang, Institute of Research and Development and Faculty Environmental of Natural Sciences, Duy Tan University, Danang, Vietnam

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Abstract

Complex transition-metal (TM) oxides, particularly the perovskite-structured compounds $R_{1-x}A_xMO_3$, where R is a lanthanide (e.g., La, Nd, Pr), A is an alkaline earth metal (e.g., Ca, Sr, Ba), and M is a transition metal (e.g., Mn, Co, Fe), represent a unique family of materials combining immense technological importance and fascinating physical phenomena originating from coupled structural, electronic and magnetic degrees of freedom. In this article, we present an introduction to the physics of perovskite transition-metal oxides, with a focus on manganites. The microscopic mechanisms that determine the magnetic and associated physical properties of the perovskite TM oxides have been analyzed in terms of the results obtained from neutron diffraction measurements and complementary techniques.

Introduction

Complex transition-metal (TM) oxides, particularly the perovskite-structured compounds $R_{1-x}A_xMO_3$, where R typically is a lanthanide, A an alkaline earth metal, and M a transition metal, have been the subject of extensive research for many decades due to their outstanding physical properties and potential applications in electronics and spintronics, data storage devices, and renewable energy and catalysis (Zaanan *et al.*, 1985; Imada, Fujimori and Tokura, 1998; Okamoto and Millis, 2004; Raveau, 2005; Pentcheva and Pickett, 2007). From the fundamental point of view, these materials are of particular interest as they show rich and complex phase diagrams highlighting a broad variety of structural, magnetic, charge ordered, and orbital ordered phases, as well as numerous intriguing physical phenomena, including the giant magnetoresistance, magnetoelectric and magnetocaloric effects, spin crossover, superionic conductivity, etc. (Zaanan *et al.*, 1985; Imada *et al.*, 1998; Okamoto and Millis, 2004; Pentcheva and Pickett, 2007). The complex nature of competing magnetic interactions, coupled to charge, lattice and orbital degrees of freedom, engaged with a simple perovskite-type crystal structure, makes $R_{1-x}A_xMO_3$ an excellent model platform for probing spin-dependent phenomena in strongly correlated magnetic systems.

To explore the nature of the emergent phenomena of strongly correlated perovskite TM oxides, one needs an approach that allows decoupling important factors among others, contributing to the physical properties. For this purpose, exploring how structural, magnetic, and other physical properties of the materials respond to variations in chemical composition, thermodynamic parameters such as temperature, magnetic field, or pressure is essential. It is worth noting that the application of high external pressure is considered one of the most appropriate tools to probe the response of physical properties of a material up on modification of structural parameters, including interatomic distances and angles. On the other hand, neutron diffraction is widely known as an advanced characterization technique that allows us to determine simultaneously both spin arrangement and crystal structure characteristics of magnetic materials like manganites, including bond angles and bond lengths in MO_6 octahedral units, as well as attributes of charge and orbital ordering. A combination of high-pressure and neutron diffraction studies will thus provide a unique opportunity to reveal the microscopic mechanisms of the spin-dependent phenomena in these strongly correlated magnetic systems.

In this article, we present an overview of the physics of complex perovskite-type oxides, with a focus on manganites, and interpret their interrelated structural and magnetic properties, based on the results of neutron diffraction studies. The microscopic mechanisms that determine their magnetic and relevant physical properties have been discussed in detail. The knowledge of these mechanisms establishes a platform for exploring functionalities in emergent magnetic oxide materials and heterostructures for application in next-generation electronic and spintronic devices.

Fundamental Aspects of Perovskite Transition Metal Oxides

Structural Arrangements in Perovskite-Type Complex Oxides $R_{1-x}A_xMO_3$

The most common structure of complex transition metal oxides of $R_{1-x}A_xMO_3$ (R - rare earth elements, A - alkaline earth elements, M - transition metal) is perovskite-type, which consists of corner-sharing oxygen octahedra MO_6 with (R,A) ions located in the spaces between them. The stability of the perovskite structure is governed by the relative sizes of atoms involved, which can be quantified using the Goldschmidt tolerance factor (Glazer, 1975; Woodward, 1997; Stokes *et al.*, 2002; Lufaso and Woodward, 2004):

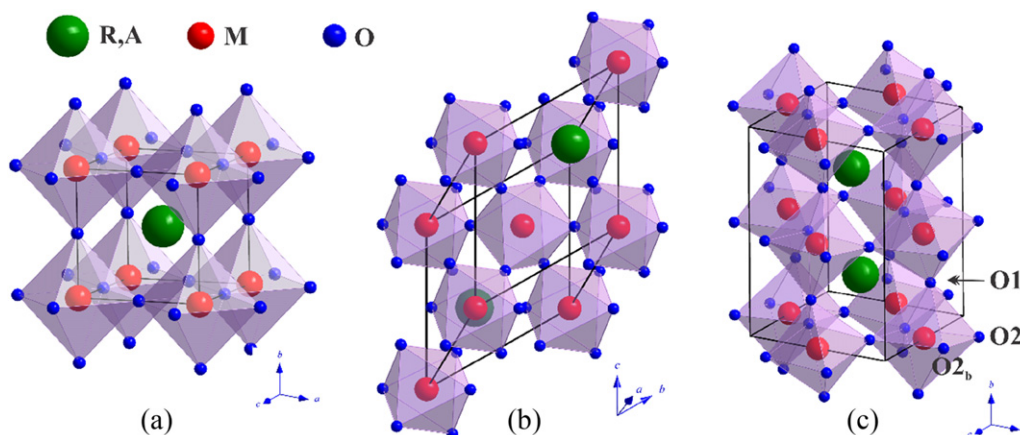


Fig. 1 Scheme of *Pm-3m* cubic (a), *R-3c* rhombohedral, and *Pnma* orthorhombic (c) perovskite-type structures.

$$t = (r_{(R,A)} + r_O) / [(r_M + r_O)], \quad (1)$$

where $r_{(R,A)} = (1-x) \cdot r_R + x \cdot r_A$ is the mean ion radius of R and A cations at the A site, r_M and r_O are the ion radius of transitional metal and oxygen atoms, respectively. For perovskite-type structures, the tolerance factor ranges from 0.78 to 1.05 (Glazer, 1975; Woodward, 1997; Stokes *et al.*, 2002; Lufaso and Woodward, 2004). The ideal *Pm-3m* cubic structure with identical M-O and M-O-M is realized only in a small number of perovskites as t is equal to or greater than unity (Glazer, 1975; Woodward, 1997; Stokes *et al.*, 2002; Lufaso and Woodward, 2004). In the cubic structure, all M-O bonds and M-O-M angles are identical, and the value of M-O-M bond angle is 180° (Fig. 1(a)). The cubic structure has been observed in $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x > 0.7$), $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, and $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x > 0.9$) (Hays *et al.*, 1999; Chmaissem *et al.*, 2003). As $t < 1$, the mismatch between $r_{(R,A)}$ and A-site space leads to a cooperative tilting of the oxygen octahedra, lowering the crystal symmetry. Numerous crystal structures with different combinations of tilting of undistorted oxygen octahedra relative to the crystallographic axes have been predicted (Glazer, 1975; Woodward, 1997; Stokes *et al.*, 2002; Lufaso and Woodward, 2004). Furthermore, the crystal symmetry can be also lowered by the cooperative Jahn-Teller (JT) distortions of the oxygen octahedra due to the presence of JT ions such as Mn^{3+} and Cu^{2+} (Stokes *et al.*, 2002; Lufaso and Woodward, 2004).

The most commonly observed crystal structures of perovskite-type $\text{R}_{1-x}\text{A}_x\text{MO}_3$ are the rhombohedral structure of *R-3c* symmetry and the orthorhombic one of *Pnma* symmetry, whose structural schemes are also shown in Fig. 1(b) and (c), respectively. As it can be seen in the phase diagram of undoped transition-metal oxides RMO_3 (Fig. 2), the *R-3c* rhombohedral structure is realized in the narrow range of $0.92 < t < 0.93$, while at smaller values of t , the *Pnma* orthorhombic one is stabilized. In the *R-3c* rhombohedral structure, the lattice parameters are $a = b = c \approx \sqrt{2}a_p$, and $\alpha \approx 60^\circ$. Moreover, the oxygen octahedra in this structure remain regular with the identical M-O bonds and M-O-M angles, but the value of M-O-M angle differs from the ideal value of 180° . This structure has been observed for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.15 < x < 0.5$), $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x < 0.5$), $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($0.33 < x < 0.67$), LaNiO_3 , and LaCoO_3 (Medarde, 1997; Blasco *et al.*, 2008). In the case of the *Pnma* orthorhombic structure, the lattice parameters are $a \approx c \approx \sqrt{2}a_p$ and $b \approx 2a_p$, and the distorted oxygen octahedra contain non-equivalent M-O bonds: one pair of apical M-O1 along the b axis and two M-O2_{a,b} pairs in the (ac) planes, which leads to the presence of two non-equivalent bond angles M-O1-M and M-O2-M (Goodenough, 1955). The anisotropy of the oxygen octahedra in this structure allows the realization of static cooperative Jahn-Teller effects. The *Pnma* structure has also been observed in various systems such as RMnO_3 ($\text{R} = \text{La-Tb}$), $\text{R}_{1-x}\text{Ca}_x\text{MnO}_3$ ($\text{R} = \text{La, Pr, Nd, Sm}$) (Goodenough, 1955; Coey *et al.*, 1999), $\text{R}_{1-x}\text{Ca}_x\text{CoO}_3$ ($\text{R} = \text{La, } 0.3 < x < 0.5, \text{ R} = \text{Pr, } x < 0.5$) (Toshiaki *et al.*, 2004; Mastinet *et al.*, 2006), RVO_3 (Martínez-Lope *et al.*, 2008), RCrO_3 (Zhou *et al.*, 2010), RFeO_3 (Marezio *et al.*, 1970), and RNiO_3 ($\text{R} = \text{Pr-Dy}$) (Medarde, 1997).

Additionally, the dependences of the average M-O bond length $d_{\langle \text{M-O} \rangle}$ and M-O-M bond angle $\varphi_{\langle \text{M-O-M} \rangle}$ on the tolerance factor t of RMO_3 compounds, calculated from the data of references Marezio *et al.* (1970); García-Muñoz *et al.* (1992); Rodríguez-Carvajal *et al.* (1998b); Alonso *et al.* (2000b); Radaelli and Cheong (2002); Cwik *et al.* (2003); Komarek *et al.* (2007) and Zhou *et al.* (2010), are shown in Fig. 3(a) and (b), respectively.

Interestingly, the average bond angle demonstrates a general trend for all compounds. In detail, it decreases nonlinearly with decreasing the tolerance factor, which can be approximated as:

$$\varphi_{\langle \text{M-O-M} \rangle} (^\circ) = 1398 - 3100t + 1911t^2. \quad (2)$$

On the other hand, the t -dependent curves of the average Mn-O bond length $d_{\langle \text{M-O} \rangle}$ are different depending on the M ion. The variation in $d_{\langle \text{M-O} \rangle}$ with t is insignificant for the RMO_3 compounds with large ion radii of $\text{R} = \text{Ti, V, Mn, and Fe}$ and becomes more pronounced for smaller ionic radii of $\text{R} = \text{Cr, Co and Ni}$. In RCrO_3 , it has been observed that $d_{\langle \text{M-O} \rangle}$ increases from 1.973 Å for $\text{R} = \text{La}$ to 1.982 Å for $\text{R} = \text{Y}$. In RCoO_3 , along with the tolerance factor, a crossover between spin states of Co^{3+} ions also contributes to variation of the structural parameters (Radaelli and Cheong, 2002; Knížek *et al.*, 2005). As a result, $d_{\langle \text{M-O} \rangle}$ decreases first from 1.934 to 1.928 Å in the range of $t = 0.920-0.902$ ($\text{R} = \text{La-Nd}$) and then increases to 1.936 Å with further

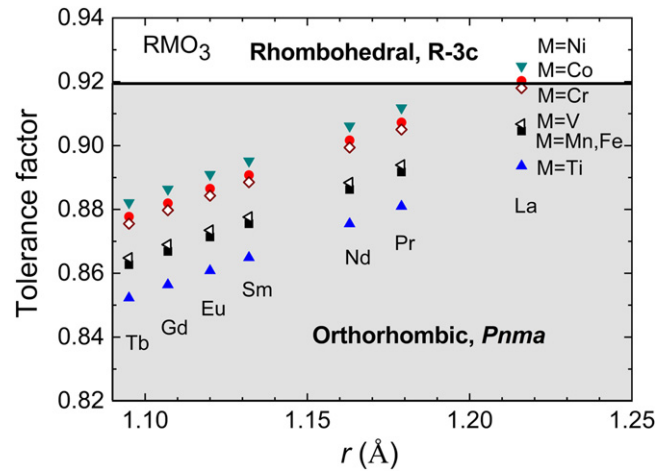


Fig. 2 Structural phase diagram of RMO_3 as a function of the tolerance factor.

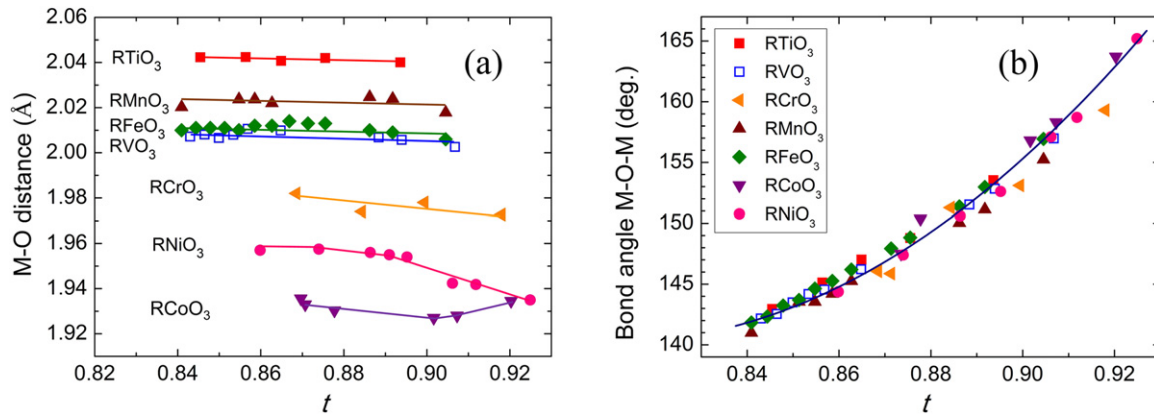


Fig. 3 Dependences of average M-O bond length (a), and M-O-M bond angle (b) of RMO_3 on the tolerance factor.

decreasing t down to 0.87 ($R = \text{Ho}$). The most pronounced change in $d_{\text{M-O}}$ has been observed in RNiO_3 , which can be attributed to the effect of partial charge disproportionation (Medarde, 1997; Alonso *et al.*, 2000a).

Magnetic Interactions and Orderings in Manganites

Superexchange

In perovskite-type transition metal oxides RMO_3 , due to large distances between neighboring transition metal magnetic ions of about 3.8–4 Å and the strong localization of 3d electron wave functions, direct magnetic exchange is typically very weak. However, 3d orbitals of cations overlap strongly with 2p orbitals of the neighboring oxygen anions. The magnetic interaction between adjacent transition-metal spins can be realized via virtual electron transfer through intermediate oxygen ions, which is called superexchange (Goodenough, 1955; Kanamori, 1959). The magnitude of the superexchange interaction J_{SE} is of the order

$$J_{\text{SE}} = 2b^2/U \quad (3)$$

where b is the d electron transfer integral ($b = b_{\text{p-d}}^2/\Delta_{\text{p-d}}$, where $b_{\text{p-d}}$ is the p - d electron transfer integral and $\Delta_{\text{p-d}}$ is the electron transfer energy from p level of ligand ion to d level of magnetic ion), U is the on-site 3d Coulomb interaction, corresponding to change in the electron configuration at the virtual electron transfer $d^n \rightarrow d^{n+1}$ (Anderson, 1959). The sign and strength of the superexchange (SE) interaction is very sensitive to such factors as the orbital state of the cations, the bond geometry, and the electronic structure as described by the empirical Goodenough-Kanamori-Anderson (GKA) rules (Goodenough, 1955; Anderson, 1959; Kanamori, 1959). According to the rules, the SE interaction is AFM in the case of a significant overlap integral between the 3d orbitals of two magnetic ions ($\angle e_g\text{-O-}e_g = 180^\circ$, $\angle t_{2g}\text{-O-}t_{2g} = 180^\circ$, $\angle t_{2g}\text{-O-}e_g = 90^\circ$). When two cations have a combination of significant and no/weak overlap integral or both cations have no/weak overlap integrals between half-filled 3d orbitals ($\angle t_{2g}\text{-O-}e_g = 180^\circ$, $\angle e_g\text{-O-}e_g = 90^\circ$, $\angle t_{2g}\text{-O-}t_{2g} = 90^\circ$), the SE interaction is ferromagnetic with a weaker strength.

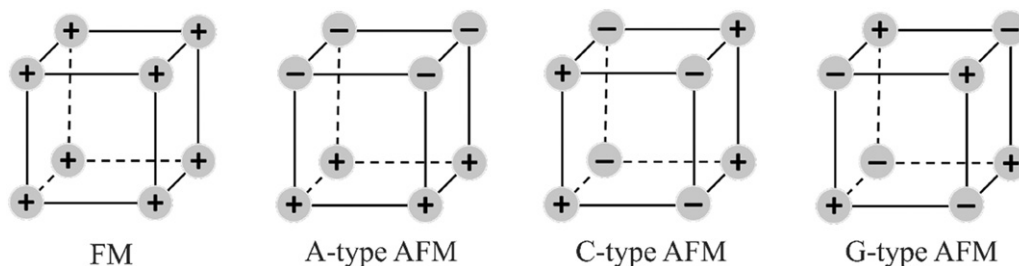


Fig. 4 Spin arrangement in FM, A-type AFM, C-type AFM, and G-type AFM orders, presented in a simple perovskite subcell. The (+) and (−) signs represent the parallel and antiparallel orientation of spins.

Double exchange

The concept of double exchange (DE) was first proposed by Zener (1951) for explaining ferromagnetism associated with high metallic conductivity in mixed-valence manganites $R_{1-x}A_x[(Mn^{3+})_{1-x}(Mn^{4+})_xO_3]$. In this concept, the e_g electron in the Mn^{3+} ions is delocalized and it can hop between two neighboring Mn cations through intermediate O^{2-} ion. During this process, its spin will interact with those of both localized t_{2g} spins, which mediates the indirect exchange between them (Zener, 1951; Anderson and Hasegawa, 1955; De Gennes, 1960). However, due to the strong intra-atomic exchange interaction, the e_g spins will be coupled ferromagnetically to the t_{2g} spins of transition metal ions involved. Therefore, it is energetically favorable for e_g electron hopping between neighboring Mn cations only if their spins are parallel and ferromagnetic alignment of neighboring spins minimizes kinetic energy. Furthermore, the DE energy is found to be dependent on the canting angle θ between the neighboring ionic spins as follows:

$$\Delta E_{DE} = -2b\cos(\theta/2) \quad (4)$$

The value $b_{\text{eff}} = b\cos(\theta/2)$ can be considered as the effective charge transfer integral, which becomes maximum for the parallel alignment of neighboring ionic spins and vanishes for their antiparallel alignment (Anderson and Hasegawa, 1955; De Gennes, 1960).

Long-range magnetic orders in manganites

It can be noticed from the Eqs. (2) and (3) that the DE and SE interactions depend, in a different manner, on the charge transfer integral b , which is controlled by M-O bond lengths and M-O-M bond angles. Therefore, variation of the structural parameters, caused by chemical doping or external pressures, may change a balance between these competing magnetic interactions and hence magnetic orderings. Wollan and Koehler (1955), when analyzing the symmetry of the magnetic ordering of $La_{1-x}Ca_xMnO_3$ manganites, proposed seven possible magnetic structures for a perovskite-like lattice (labeled as A, B, C, D, E, F, G) and their combinations. Using the magnetic representation analysis, Bertaut (1963) pointed out that for the propagation vector $\mathbf{k} = 0$, only four main magnetic orders (FM, A-, C- and G-type AFM), as illustrated in Fig. 4, can be realized in the $Pnma$ orthorhombic crystal structure of manganites. In addition to the simple magnetic structures, complex magnetic structures such as their combinations of the types C_xA_z , $G_zA_yF_x$, etc., and magnetic orders with other propagation vectors were observed experimentally in manganites.

Structural Refinements From Neutron Diffraction Data

As an advantage of neutron diffraction over X-ray and electron diffraction, the stochastic variation of neutron scattering length on atomic number, caused by weak interaction of neutrons with matter, makes it possible to determine accurately positions of light atoms, e.g., oxygen in complex oxides, or atoms with close atomic numbers and isotopes. More importantly, due to the existence of neutron's magnetic moment, the neutron diffraction allows one to determine directly the magnetic structure of materials (Chatterji, 2006).

The most widespread technique is the thermal neutron powder diffraction (NPD), where distribution of the scattered neutrons is registered by a detector system as a function of the scattering angle (the angle between the incident and scattered neutron beams with the same wavelength) or neutron wavelength (in time-of-flight experiments using polychromatic neutron beam and fixed scattering angles). Data refinement is typically performed using the Rietveld method, which has been widely employed as a unique tool for structural analysis of polycrystalline materials. This method consists of refining crystal and/or magnetic structures by minimizing the weighted squared difference between observed and calculated intensities of measured diffraction patterns. The calculated intensity I_{cal} is described as a sum of the contributions from neighboring Bragg reflections (Rodríguez-Carvajal, 1993):

$$I_{\text{calc}}(d_i) = \sum_i S_i \sum_H C_H |F_H|^2 R(d_H - d_i) + I_b(d_i), \quad (5)$$

where the reciprocal lattice vector H is associated with the Bragg reflections (hkl) , S_i is the scale factor of the i -th phase, C_H is the correction factor, R is the profile function approximating shape of measured Bragg reflections, I_b is the background level, and F_H is the structure factor defined by symmetry of atomic arrangement in the crystal structure and also spin arrangement, if magnetic structure is involved. In neutron diffraction, onset of the FM order is manifested as an additional contribution to intensity superimposed on nuclear Bragg peaks, while onset of the AFM one often leads to appearance of extra magnetic peaks. For magnetic

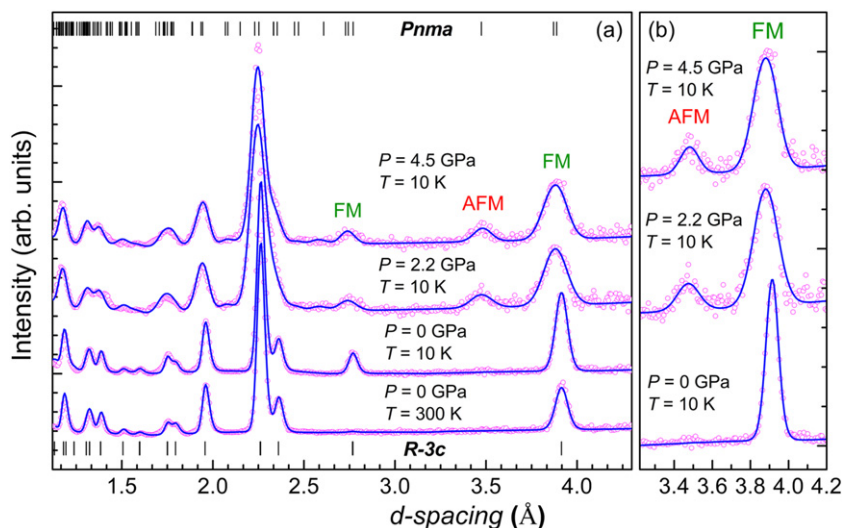


Fig. 5 Neutron diffraction patterns of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Sb}_{0.1}\text{O}_3$ collected at $T = 10$ and 300 K under different pressures and processed by the Rietveld method. Adapted with permission from Kichanov, S.E., *et al.*, 2020. Magnetic phase transition in $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Sb}_{0.1}\text{O}_3$ manganite under pressure. *Chemical Physics* 528, 110541. <https://doi.org/10.1016/j.chemphys.2019.110541>.

structure analysis, the first important step is to identify the propagation vectors k , describing the periodicity of the spin arrangement, by indexing magnetic peaks. For the set k vectors, the magnetic structure can be refined by testing different magnetic structure models given by the representation analysis. For example, the NPD patterns of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Sb}_{0.1}\text{O}_3$ collected at different pressures and low temperature are shown in Fig. 5. In the pattern at 10 K and ambient pressure, we observe a magnetic contribution to nuclear peaks located at $d = 2.76$ and 3.92 Å , indicating the onset of the FM state. At given pressures and $T = 10\text{ K}$, the purely magnetic peaks of AFM nature at $d = 3.47\text{ Å}$ were observed (Fig. 5). The data refinement has revealed that these peaks correspond to the formation of the A-type AFM order of the Mn spins.

Magnetic Phase Transitions in Manganites

Undoped Manganites RMnO_3

Undoped manganese oxides RMnO_3 are insulators and have the orthorhombic structure of $Pnma$ symmetry in accordance with the values of the tolerance factor. These compounds contain Jahn-Teller (JT) Mn^{3+} ($3d^4$, $t_{2g}^3e_g^1$) ions with a double e_g -orbital degeneracy. The realization of the static cooperative JT effect, associated with the removal of orbital degeneracy due to the occurrence of structural deformations, causes the formation of a spatial ordering of $d_{3x^2-r^2}$ and $d_{3z^2-r^2}$ orbitals oriented along the x and z unit-cell directions (Fig. 6) below the critical temperature T_{JT} (Rodríguez-Carvajal *et al.*, 1998a). The value of T_{JT} is 750 K for LaMnO_3 , which sharply increases with increasing tolerance factor and reaches $T_{\text{JT}} \sim 1500\text{ K}$ ($R = \text{Gd} - \text{Dy}$) (Zhou and Goodenough, 2006).

Based on the structural information refined from room-temperature NPD data, the dependences of the unit cell parameters and volume, as well as the Mn-O bond lengths and Mn-O-Mn bond angles of the RMnO_3 system (Alonso *et al.*, 2000b; Okamoto *et al.*, 2008; Uusi-Esko *et al.*, 2008; Pomjakushin *et al.*, 2009; Oliveira *et al.*, 2011) on the tolerance factor t are shown in Fig. 7. Upon decreasing t , the lattice parameters c and b ($c > b/\sqrt{2}$) gradually decrease in the entire range of the tolerance factor of $0.904 - 0.841$ ($R = \text{La} - \text{Lu}$), while the parameter a shows a maximum at $t = 0.871$ ($R = \text{Eu}$). Furthermore, due to the spatial geometry of the e_g -orbital ordering, the MnO_6 octahedra are distorted with two longest Mn-O_{2a} and shortest Mn-O_{2b} bonds in the (ac) plane and intermediate apical Mn-O₁ bond oriented perpendicular to the plane (Fig. 7). As can be seen in Fig. 7(c), as the tolerance factor t varies, the longest Mn-O_{2b} bond exhibits a similar trend as the lattice parameter a . On the other hand, the MnO₁ apical bond nonlinearly reduces, while the Mn-O_{2a} almost remains unchanged over the entire range of t . The average value of the Mn-O bond lengths of 2.02 Å remains almost unchanged with the variation of t . The bond angles, Mn-O₁-Mn and Mn-O₂-Mn, show a tendency to decrease with decreasing t . Additionally, the t -dependent curve of the Mn-O₁-Mn bond angle is linear, which differs from the Mn-O₂-Mn curve.

Fig. 8 demonstrates the magnetic phase diagram of RMnO_3 constructed based on data of references Kimura, 2003b; Hemberger *et al.*, 2004; Kimura *et al.*, 2005; Ye *et al.*, 2007; Okamoto *et al.*, 2008; Pomjakushin *et al.*, 2009; Garganourakis *et al.*, 2012 and Stewart *et al.*, 2015. In the RMnO_3 compounds with relatively high values of t ($R = \text{La-Sm}$), an AFM A-type ordering appears at low temperatures. The scheme of the A-type AFM structure is illustrated in Fig. 9(a). The Néel temperature T_N of the A-type AFM phase decreases steeply with decreasing the tolerance factor from 140 K for $R = \text{La}$ to 59 K for

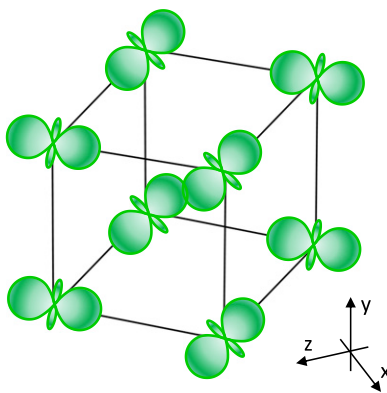


Fig. 6 Character of orbital ordering in RMnO_3 . For illustration purpose, the simple perovskite subcell and the orientation of the crystallographic axes of the orthorhombic structure are indicated.

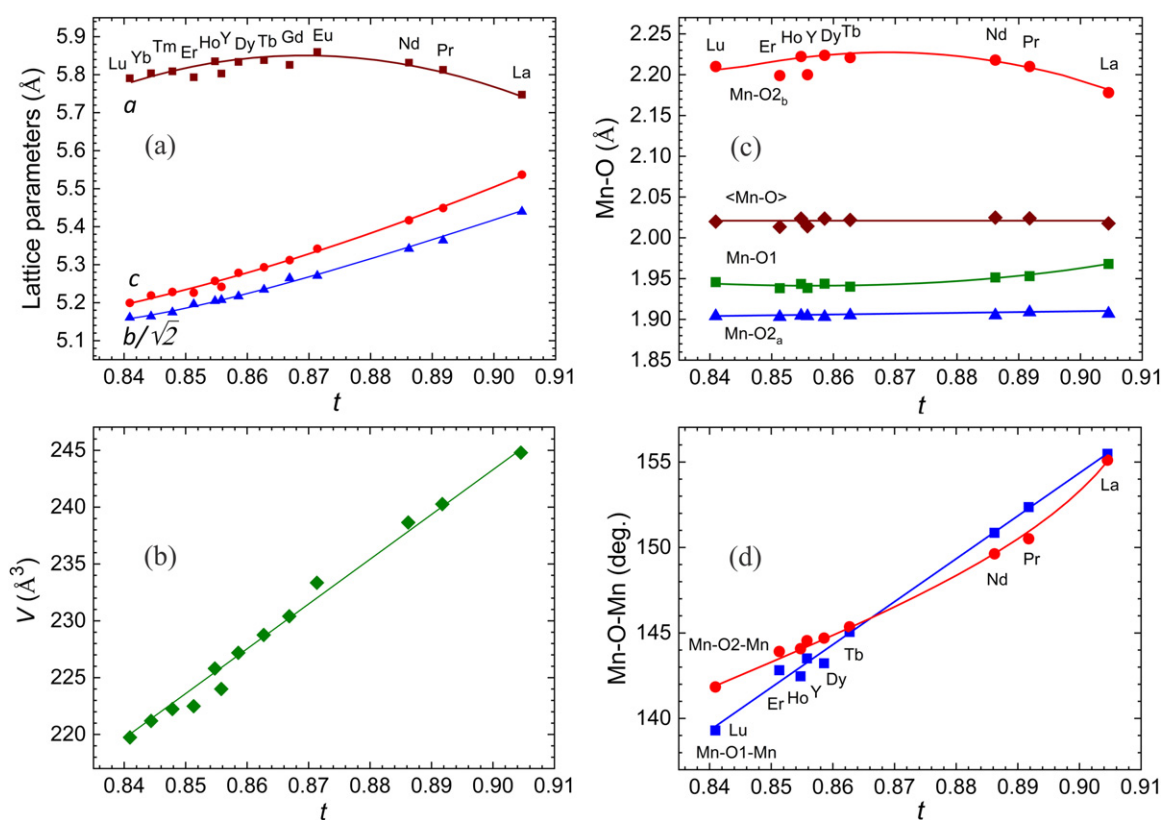


Fig. 7 Unit-cell parameters (a), volume (b), Mn-O bond length (c), and Mn-O-Mn bond angle (d) of RMnO_3 as functions of the tolerance factor t .

$R = \text{Sm}$ (see Table 1). The compounds with lower tolerance factors demonstrate a more complex incommensurate (IC) AFM order with the propagation vector $q = (q_s, 0, 0)$ with q_s ranging from 0.29 to 0.49. The value of q_s decreases with decreasing T in the temperature range $T_L < T < T_N$, and then becomes nearly constant below T_L . The magnetic structure below T_L can be either commensurate or incommensurate. For instance, $q_s = 0$ corresponding to the A-type AFM structure was reported for $R = \text{Eu, Gd}$ at $T < T_L$, while $q_s = 0.5$ corresponding to the E-type AFM structure (Fig. 9(b)) was found for $R = \text{Ho, Tm, Yb, Lu}$ (Wollan and Koehler, 1955).

Unlikely, for the compounds with $R = \text{Tb, Dy, Er}$ the AFM order remains incommensurate below $T < T_L$. In the range of $t = 0.871\text{--}0.858$ ($R = \text{Eu - Dy}$), T_N exhibits a gradual decrease from 51 to 39K, then slightly changes upon further lowering t (Fig. 8). The critical temperature T_L demonstrates an anomalous variation with t . It first sharply decreases from 46K for $R = \text{Eu}$ to 24K for $R = \text{Gd}$, then increases up to 35K for $R = \text{Lu}$. Interestingly, the presence of a small spontaneous ferroelectric polarization below T_N was found in the IC AFM or E-type AFM phase of RMnO_3 ($R = \text{Tb, Dy, Ho, Er, Tm, Yb, Lu}$) (Goto, 2004; Ishiwata, 2010; Kimura, 2003a, 2005, 2007; Pomjakushin, 2009). Its appearance is caused by lattice inversion symmetry breaking by modulated

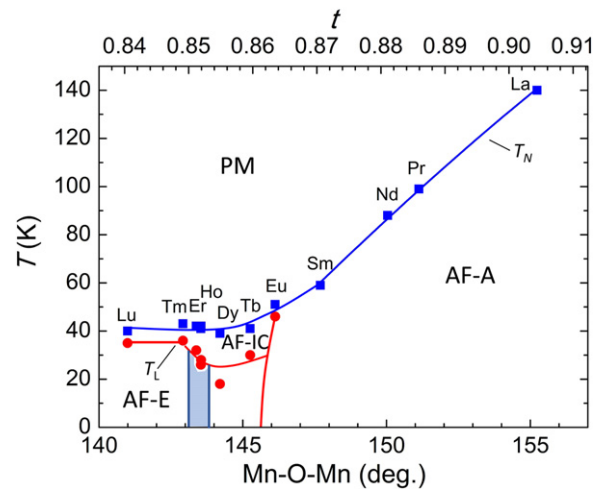


Fig. 8 Magnetic phase diagram of manganites RMnO_3 . In the shaded region, both the incommensurate AFM state (AF-IC) and the commensurate E-type AFM state (AF-E) maybe coexist.

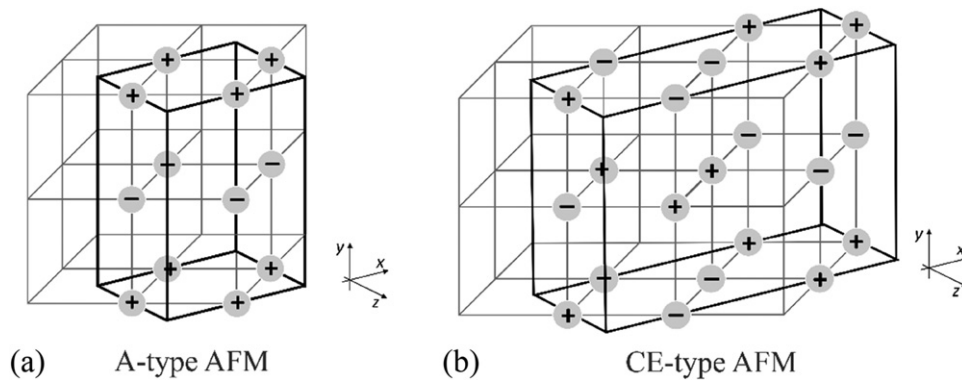


Fig. 9 A-type (a) and E-type (b) AFM order in the orthorhombic crystal structure of RMnO_3 .

Table 1 Magnetic ordering temperatures and types of magnetic order of RMnO_3 manganites

Compound	T_N (K)	T_L (K)	Type of magnetic order	References
LaMnO_3	140	—	A-type	(Wollan and Koehler, 1955)
PrMnO_3	99	—	A-type	(Hemberger <i>et al.</i> , 2004)
NdMnO_3	88	—	A-type	(Hemberger <i>et al.</i> , 2004)
SmMnO_3	59	—	A-type	(Kimura, 2003b)
EuMnO_3	51	46	IC ($T < T_N$), A-type ($T < T_L$)	(Kimura, 2003b)
GdMnO_3	43	23	IC ($T < T_N$), A-type ($T < T_L$)	(Kimura <i>et al.</i> , 2005)
TbMnO_3	41	30	IC, $q_s = 0.28$ ($T < T_L$)	(Kimura <i>et al.</i> , 2005)
DyMnO_3	39	18	IC, $q_s \approx 0.385$ ($T < T_L$)	(Kimura <i>et al.</i> , 2005)
HoMnO_3	41	26	IC ($T < T_N$), E-type ($T < T_L$)	(Kimura, 2003b)
ErMnO_3	42	28	IC, $q_s = 0.433$ ($T < T_L$)	(Ye <i>et al.</i> , 2007)
TmMnO_3	42	32	IC ($T < T_N$), E-type ($T < T_L$)	(Pomjakushin <i>et al.</i> , 2009)
YbMnO_3	43	38	IC ($T < T_N$), E-type ($T < T_L$)	(Stewart <i>et al.</i> , 2015)
LuMnO_3	40	35	IC ($T < T_N$), E-type ($T < T_L$)	(Okamoto <i>et al.</i> , 2008; Garganourakis <i>et al.</i> , 2012)

spin arrangements, (Kenzelmann *et al.*, 2005; Van Den Brink and Khomskii, 2008). Consequently, the multiferroic RMnO_3 systems exhibit a strong magnetoelectric effect.

The origin of the complex phase diagram of the RMnO_3 systems has been assumed due to the competition between FM nearest-neighbor (NN) superexchange and AFM next-nearest-neighbor (NNN) super-superexchange interactions between Mn sites in the ac planes by a combination of lattice distortion and the staggered orbital ordering (Kajimoto *et al.*, 2005; Pomjakushin *et al.*, 2009).

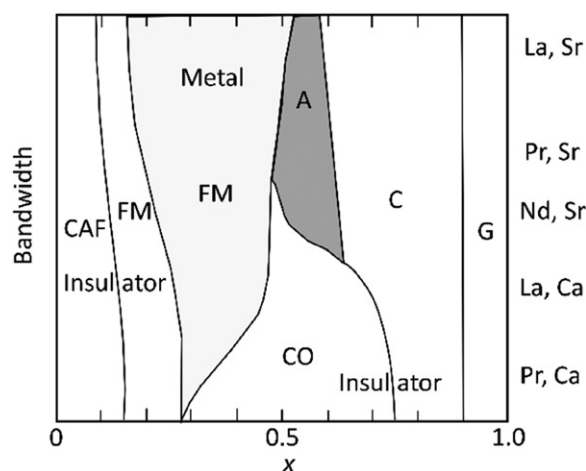


Fig. 10 Schematic phase diagram of manganites as functions of concentration of Mn^{4+} ions and charge transfer bandwidth. Adapted with permission from Kajimoto, R., *et al.*, 2002. Stripe-type charge ordering in the metallic A-type antiferromagnet $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. *Physical Review B*, 66 (18), 180402. <https://doi.org/10.1103/PhysRevB.66.180402>.

Indeed, the inelastic neutron scattering results demonstrated that for LaMnO_3 having the highest t , the strength of the J_{1-ac} interaction of 1.67 meV is the largest one, leading to formation of the in-plane FM spin arrangement. The less strong AFM superexchange interaction between the nearest-neighbor Mn sites along the b axis $J_{1-b} \approx -1.21$ meV causes the AFM stacking of adjacent spin planes in the long-range A-type AFM state (Kajimoto, 2005; Kimura, 2003b). For PrMnO_3 , the NNN exchange interaction (J_{2-ac}) within the ac planes J_{2-ac} becomes evident with the strength of -0.22 meV weaker by a factor of 5 than $J_{1-ac} = 1.12$ meV, while J_{1-b} practically keeps at the same value as for LaMnO_3 (Kajimoto *et al.*, 2005).

For lower- t TbMnO_3 , J_{1-ac} weakens significantly and becomes comparable with J_{2-ac} , $J_{1-ac} \approx 0.3$ meV, $J_{2-ac} \approx -0.15$ meV, while J_{1-b} shows a much weaker reduction, $J_{1-b} \approx -1.0$ meV (Kajimoto *et al.*, 2005). The competition between J_{1-ac} and J_{2-ac} apparently suppresses the classic spin ordering in TbMnO_3 and DyMnO_3 . The weakening in J_{1-ac} and J_{1-b} upon lowering t can be attributed to the decrease in the Mn-O-Mn bond angles (Fig. 7). The enhancement of J_{2-ac} is likely due to the shortening in O-O distance of Mn-O-O-Mn exchange pathways (Alonso, 2000b; Kimura, 2003b). Alternatively, Zhou *et al.* attributed the nature of the magnetic structure transformations in RMnO_3 to a competition between t_{2g} -orbital AFM and e_g -orbital FM superexchange interactions within each Mn-O-Mn bond in the (ac) planes (Zhou and Goodenough, 2006).

Influence of a Doping on the Magnetic Structures of $\text{R}_{1-x}\text{A}_x\text{MnO}_3$

The substitution of R^{3+} by divalent alkaline-earth cations leads to the coexistence of Mn^{3+} and Mn^{4+} ions in $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{R}_{1-x}\text{A}_x[\text{Mn}^{3+}]_{1-x}[\text{Mn}^{4+}]_x\text{O}_3$). The competition between FM double exchange interaction mediated by hopping of itinerant e_g electrons in $\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{4+}$ bonds and AFM superexchange interaction between t_{2g} localized magnetic moments coupled to lattice, electronic and orbital degrees of freedom results in a complex magnetic phase diagram of the compounds (Fig. 10) (Zener, 1951; Anderson and Hasegawa, 1955; De Gennes, 1960; Fontuberta, *et al.*, 1999; Kajimoto *et al.*, 2002). Generally, at low doping concentrations, in most of the manganites there exist canted AFM and FM insulating states below $x = 0.15\text{--}0.22$. In the concentration range $\sim 0.15\text{--}0.2 < x < 0.5$, the DE interaction becomes dominant, which leads to the transition to the metallic FM state with $T_C \approx T_{IM}$ (Zener, 1951; Coey *et al.*, 1999; Salamon and Jaime, 2001). T_C and T_{IM} reach a maximum at an optimal doping level of $x \sim 0.3\text{--}0.35$.

Figs. 11 and 12 present the dependence of the unit-cell parameters, Mn-O bond lengths and Mn-O-Mn bond angles of the optimally doped $\text{R}_{0.7}\text{A}_{0.3}\text{MnO}_3$ manganites on the tolerance factor t , plotted based on the structural data of references Millange *et al.* (1996); Hibble *et al.* (1999); Radaelli *et al.* (2001); Boujelben *et al.* (2002) and Kozlenko *et al.* (2004). It can be seen that the lowering of the concentration of Mn^{3+} Jahn-Teller ions leads to a significant decrease of structural distortions in $\text{R}_{0.7}\text{A}_{0.3}\text{MnO}_3$ manganites compared to the undoped ones. The difference between the reduced unit-cell parameters a , $b/\sqrt{2}$, and c does not exceed 1.5%. As the tolerance factor decreases, the lattice parameter a increases nonlinearly, while both parameters $b/\sqrt{2}$ and c decrease consistently and become close in value for low- t compounds such as $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$.

The dependence of the particular Mn-O bond lengths on the tolerance factor of orthorhombic $\text{R}_{0.7}\text{A}_{0.3}\text{MnO}_3$ manganites follow the behavior of relevant lattice parameters (Fig. 12(a)). As the tolerance factor decreases, a distortion between the in-plane bonds develops rapidly, resulting in a noticeable increase of the Mn-O_{2b} bond and a decrease of the Mn-O_{2a} . The Mn-O_1 bond length varies more weakly. It first increases as t decreases down to 0.916 ($\text{R} = \text{La, Ca}$), and then slightly decreases upon further lowering t . The observed distortion geometry at sufficiently low t values resembles qualitatively those of undoped RMnO_3 systems (Fig. 7) and points to the progressive growth of JT distortions. Nevertheless, there is a difference between the shortest Mn-O_{2a} and longest Mn-O_{2b} bonds of about 2.5% that remains about five times less with respect to that of RMnO_3 . Furthermore, upon decreasing the

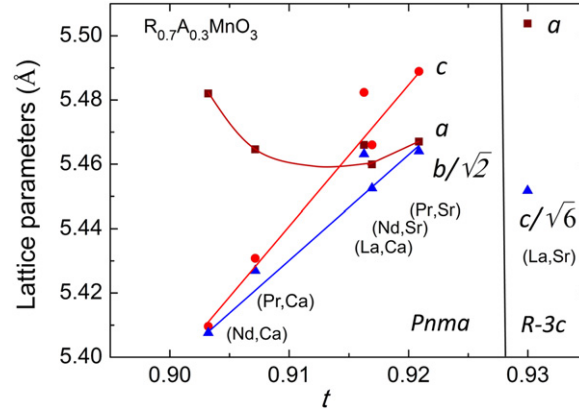


Fig. 11 Lattice parameters of $R_{0.7}A_{0.3}\text{MnO}_3$ as functions of the tolerance factor t .

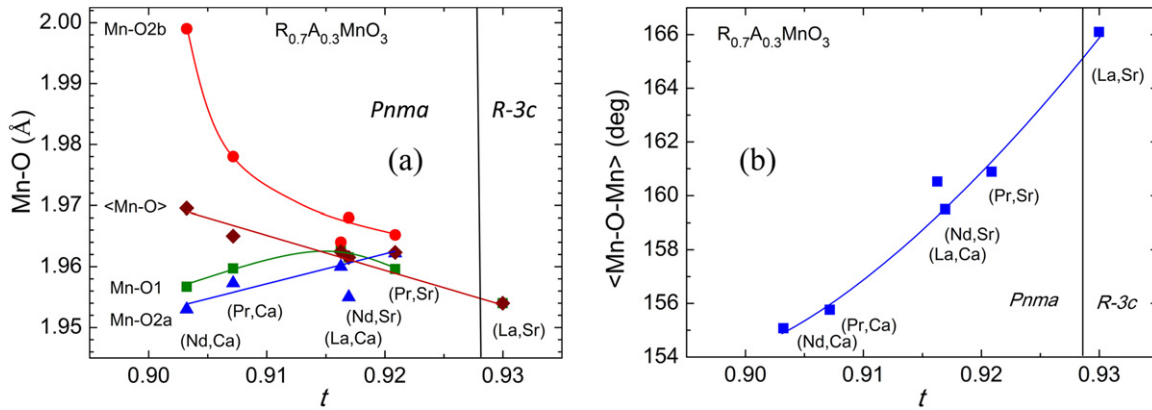


Fig. 12 Mn-O bond length (a) and Mn-O-Mn bond angle (b) of $R_{0.7}A_{0.3}\text{MnO}_3$ as functions of the tolerance factor t .

tolerance factor, the average Mn-O bond length increases almost linearly from 1.954 (La,Sr) to 1.969 Å (Nd,Ca), while the average Mn-O-Mn bond angle decreases from 166.1 (La,Sr) to 155.1° (Nd,Ca) (Fig. 12(b)).

In the framework of the DE theory, the Curie temperature of the FM phase of manganites is proportional to the charge carrier bandwidth (Anderson and Hasegawa, 1955; De Gennes, 1960; Coey *et al.*, 1999; Dagotto *et al.*, 2001):

$$T_c \sim W \sim \frac{\cos^2 \langle \varphi \rangle}{\langle l \rangle^{3.5}}, \quad (6)$$

From the t -dependent data of the mean $\langle \text{Mn-O} \rangle$ ($\langle l \rangle$) and Mn-O-Mn ($\langle \varphi \rangle$) parameters of $R_{0.7}A_{0.3}\text{MnO}_3$, it has been demonstrated that variation of these structural parameters causes a decrease of T_c by about 20% with decreasing t from 0.93 ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) to 0.093 ($\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$). It is in sharp contrast to the experimentally observed significant decrease of T_c by about 4 times from 370K for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ to 95K for $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (Vasiliu-Doloc *et al.*, 1998; Ye *et al.*, 2006; Zhang *et al.*, 2007). Furthermore, as shown by inelastic neutron scattering measurements, the exchange integral of the nearest-neighbor FM interaction decreases by about 20% from $J_1 = 2.5$ meV in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ to 2.0 meV in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (for the FM phase stabilized upon cooling in an external magnetic field of 5 T) (Vasiliu-Doloc *et al.*, 1998; Ye *et al.*, 2006; Zhang *et al.*, 2007). These above arguments clearly demonstrate the strong role of the electron-phonon interaction associated with the JT distortions in the magnetic properties of the $Pnma$ orthorhombic manganites. It has been shown that presence of the cooperative JT distortions of the oxygen octahedra leads to formation of polarons and to an effective change in the bandwidth (Millis *et al.*, 1995; Zhao *et al.*, 1996; Mira *et al.*, 2002):

$$W \sim W_0 \exp(-\gamma E_{JT}/\hbar) \quad (7)$$

where the polaron binding energy E_{JT} is scaled by the distortion degree of the oxygen octahedra (Kozlenko and Savenko, 2004), ω is the frequency of the phonon oscillation mode of oxygen octahedra, and γ ($0 < \gamma < 1$) is the electron-phonon coupling parameter. The value of $\gamma E_{JT}/\hbar\omega$ was found to increase with decreasing t (Fontcuberta *et al.*, 1999).

As the concentration of JT Mn^{3+} ions decreases, the AFM superexchange interaction between the Mn magnetic moments formed by localized t_{2g} electrons becomes dominant in the $R_{1-x}A_x\text{MnO}_3$ compounds with $x > 0.5$. For compounds with large mean ion radius of (R,A) cations such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$, and $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$, a general sequence of magnetic phase

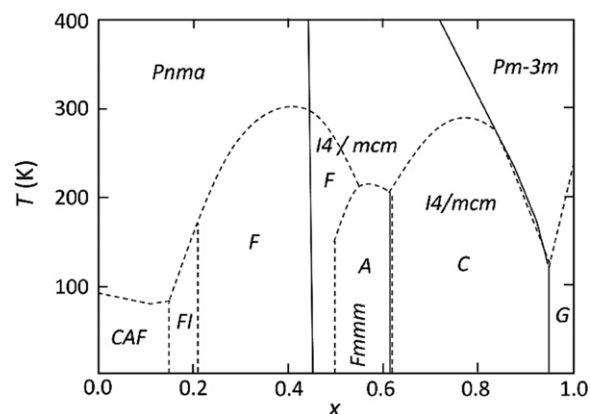


Fig. 13 The structural (solid lines) and magnetic (dash lines) phase diagram of $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$.

transitions was observed with increasing x in the range of $0.5 < x < 1.0$: FM (metallic) $\rightarrow$ A-type AFM (metallic) $\rightarrow$ C-type AFM (insulating) $\rightarrow$ G-type AFM (insulating) (Urushibara *et al.*, 1995; Liu *et al.*, 2001; Chmaissem *et al.*, 2003; Knížek *et al.*, 2004). For demonstration, the structural and magnetic phase diagram of $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$, constructed based on data of references Chmaissem *et al.* (2003) and Knížek *et al.* (2004), is shown in Fig. 13. Moreover, it should be noted that the A-type AFM state in these doped manganites is quasi-two dimensional metallic with the $d_{x^2-y^2}$ e_g orbital ordering, which differs from the another insulating A-type AFM state with the antiferrodistortive ordering of $d_{3x^2-r^2}/d_{3z^2-r^2}$ orbitals in the undoped RMnO_3 (Rodríguez-Carvajal *et al.*, 1998a; Kajimoto *et al.*, 1999; Alonso *et al.*, 2000b; Jirák *et al.*, 2000; Chatterji *et al.*, 2003).

As the average radius of (R,A) cations $r_{(R,A)}$ decreases, the structural distortion degree of the oxygen octahedra as well as the localization tendency of e_g electrons increases, leading to the formation of complex AFM states with orbital and charge (CO) ordering of Mn^{3+} and Mn^{4+} ions in the manganites having a smaller mean radii of the R,A cations (smaller carrier bandwidth W) such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$, and $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$. Fig. 14 shows the magnetic phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ constructed based on data of references Schiffer *et al.* (1995); Millis (1998); Dolinsek *et al.* (2000) and Pissas and Kallias (2003). Similar to the previous cases, there exist insulator canted AFM, FM, and metallic FM states in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ with at $x < 0.5$. In the $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ compound, at temperature $T_{\text{CO}} \approx T_N \approx 160\text{K}$ an AFM state of the so-called CE type with the charge and orbital ordering of the Mn^{3+} and Mn^{4+} ions with the respective propagation vectors $q_1 = (0\ 0\ 1/2)$ and $q_2 = (1/2\ 0\ 1/2)$ is formed (Fig. 15(a)). The CE-type AFM state exists in the concentration range of $0.5 < x < 0.63$. At the special concentration ratios of $\text{Mn}^{3+}:\text{Mn}^{4+}$ of 1:2 ($x = 2/3$) and 1:3 ($x = 3/4$), one observed the formation of more complex AFM orderings: AF-2/3 with the propagation vector $k_{2/3} = (1/3\ 0\ 1/2)$ (Fig. 15(b)) and AF-3/4 with the propagation vector $k_{3/4} = (1/4\ 0\ 1/2)$ in $\text{La}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$ and $\text{La}_{1/4}\text{Ca}_{3/4}\text{MnO}_3$, respectively (Marezio, 1999; Pissas and Kallias, 2003; Pissas *et al.*, 2005). With increasing the concentration of Mn^{4+} ions, the temperature of charge and orbital ordering sharply increases and reaches a maximum $T_{\text{CO}} \approx 270\text{K}$ at $x \sim 0.65$. On the contrary, the Néel temperature decreases to $T_N \approx 150\text{K}$ at $x \sim 0.65$, and then increases to 200K at $x \sim 0.8$, corresponding to the C-type AFM phase boundary.

The formation of the charge and orbital ordered phases in the concentration range of $x \geq 0.5$ is accompanied by monoclinic distortions of the crystal structure (Marezio, 1999; Pissas *et al.*, 2005). In $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ at $T < T_{\text{CO}}$, the oxygen octahedra in the Mn^{3+} sublattice have a pronounced JT distortion with two long Mn-O bond lengths of 2.07Å and four short bond lengths of 1.92Å . The oxygen octahedra in the Mn^{4+} sublattice remain almost isotropic with nearly equal Mn-O bond lengths of 1.91Å (Radaelli *et al.*, 1997). In $\text{La}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$ at $T < T_{\text{CO}}$ the oxygen octahedra in the Mn^{3+} sublattice exhibit a similar distortion with two long Mn-O bonds of 2.02Å and four short bonds of 1.91Å . Meanwhile, the oxygen octahedra in the Mn^{4+} sublattices are more distorted with five approximately identical Mn-O bonds of about 1.9Å and one long bond of about 2.0Å , which may be due to the frustration in magnetic interactions between Mn spins (Marezio, 1999). With a further increase in the concentration of Mn^{4+} ions, the C-type AFM state forms in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x > 0.79$. Unlike the C-type AFM phase in the tetragonal compounds of $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$, in the C-type AFM structure of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ the magnetic moments of Mn ions are located in the (*ac*) planes and form FM chains along the $[1\ 0\ 1]$ direction, which are reversed in the antiparallel orientation in neighboring chains. At $x > 0.85$, the G-type AFM phase is observed, which coexists with the C-type AFM phase up to $x < 0.95$. In the regions of the C- and G-type AFM phases, increasing the Mn^{4+} concentration leads to a significant decrease in the Néel temperature from $T_N \approx 200\text{K}$ ($x \sim 0.8$) to 120K ($x = 1$).

In $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ manganites, a further decrease in the average radius of the (R,A) cation enhances the tendency towards charge localization and a decrease in the charge transfer bandwidth. Therefore, the FM metallic state is absent in the phase diagram of these compounds, whereas the regions of the FM and charge-ordered AFM insulating states expand. At $x > 0.3$, increasing x leads a consequent change in the magnetic ground state: pseudo-CE type AFM at $0.3 < x < 0.4$, CE-type AFM at $x \geq 0.4$, and more complex AFM states at $x > 0.5$ (Jirák *et al.*, 1985, 2002). The main difference between the pseudo-CE and CE-type AFM structures lies in the parallel and antiparallel orientation of the magnetic moments in adjacent (*ac*) planes. In the concentration range $x > 0.9$, a complex inhomogeneous magnetic state with the presence of FM regions embedded in the G-type AFM matrix is observed in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ manganites (Savosta *et al.*, 2000).

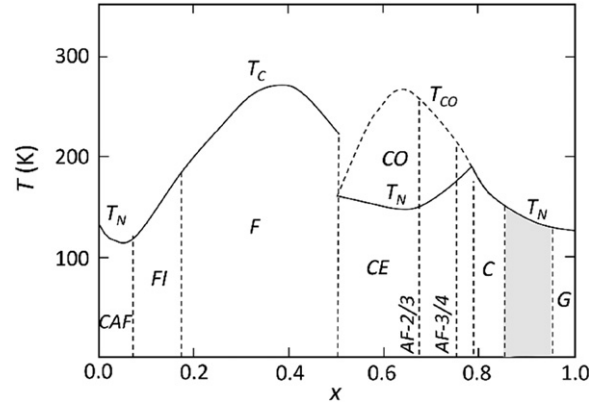


Fig. 14 Magnetic phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$.

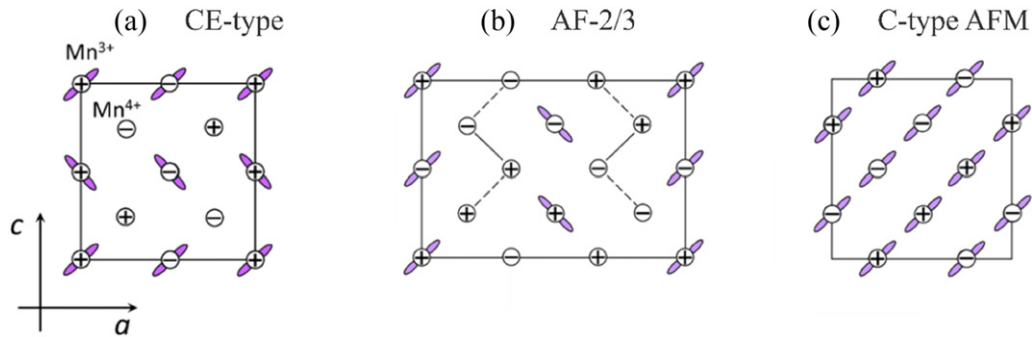


Fig. 15 Spin, charge and orbital orderings in the CE, AF-2/3 and C-type AFM phases of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ in the plane (ac). The direction of the magnetic moments is reversed in adjacent planes along the b axis.

High-Pressure Effects on the Crystal and Magnetic Structures of Manganites

Neutron diffraction studies have shown that in LaMnO_3 the initial A-type AFM structure is maintained at pressures up to 6.7 GPa but with a reorientation of the ordered magnetic moments (Pinsard-Gaudart *et al.*, 2001). The magnetic ordering temperature of the A-type AFM phase in LaMnO_3 increases upon compression with a pressure coefficient of $(1/T_N)dT_N/dP = 0.039 \text{ GPa}^{-1}$, accompanied by shortening of Mn-O distances and broadening of Mn-O-Mn angles. Indeed, the room-temperature average Mn-O bond length almost linearly decreases with a pressure coefficient of $k_l = -(1/l_0)(dl/dP) \approx 0.0032 \text{ GPa}^{-1}$, while the average Mn-O-Mn bond angle gradually increases from ≈ 155.2 – 157.6° under high pressures up to 6.6 GPa. A similar pressure-induced effect has been observed for other RMnO_3 manganites showing the A-type AFM order, in which the pressure coefficient decreases with decreasing the R^{3+} ion size. The value of $(1/T_N)dT_N/dP$ is 0.029 and 0.019 GPa^{-1} for PrMnO_3 and SmMnO_3 , respectively (Zhou and Goodenough, 2003). Above 7 GPa, the signatures of pressure-induced instability of the A-type AFM phase of LaMnO_3 were revealed (Pinsard-Gaudart *et al.*, 2001), whose origin can be attributed to the suppression of the cooperative JT effect and the concomitant orbital ordering (Loa *et al.*, 2001).

In TbMnO_3 , applied pressure up to 3.6 GPa suppresses the initial IC AFM structure and induces an onset of the E-type commensurate AFM order in the Mn magnetic sublattice. Moreover, the magnetic ordering in the Tb^{3+} sublattice changes from short-range to long-range under compression (Makarova *et al.*, 2011). Additionally, the Néel temperature of the Mn magnetic sublattice significantly decreases under pressure with a coefficient $(1/T_N)dT_N/dP = -0.099 \text{ GPa}^{-1}$, whereas that of the Tb magnetic sublattice increases with $(1/T_N)dT_N/dP = 0.24 \text{ GPa}^{-1}$. The origin of the pressure-induced magnetic transformations of the Mn sublattice is directly related to the enhancement of the J_{2-ac}/J_{1-ac} ratio (Makarova *et al.*, 2011). Furthermore, the applied pressure induces a flop of the ferroelectric polarization, which reaches to the maximum $P \approx 1.0 \mu\text{C cm}^{-2}$ at 5.2 GPa (Aoyama *et al.*, 2014). The observed value is larger by an order of magnitude than those ever reported in spin-driven ferroelectrics (Aoyama *et al.*, 2014).

For $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ manganites, application of pressure causes a large number of magnetic phase transitions. The microscopic mechanisms of these transitions are associated with a pressure-tuned anisotropic distortion of oxygen octahedra, mediating features of the e_g orbital polarization and balance of the competing magnetic interactions along different crystallographic directions. In the case of the rhombohedral $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ compound with a symmetric MnO_6 octahedra, the FM metallic phase remains stable under pressures up to 8 GPa. The Curie temperature linearly increases upon compression with a pressure coefficient $dT_C/dP = 4.3 \text{ K/GPa}$ (Kozlenko *et al.*, 2004). From the Eq. (6), the relative change of T_C upon compression can be presented as:

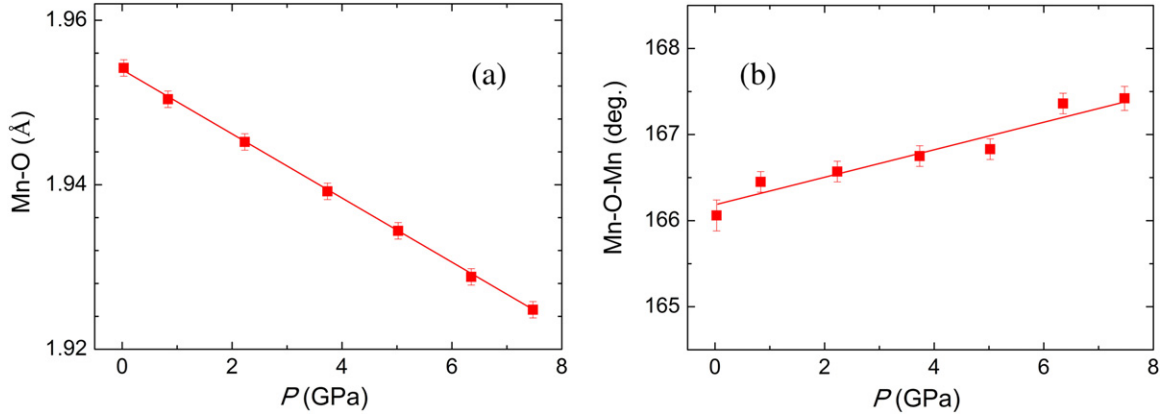


Fig. 16 Pressure dependences of Mn-O bond length (a) and Mn-O-Mn bond angle (b) in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$.

$$(1/T_C)(dT_C/dP) = 3.5k_l - 2\varphi \cdot \tan(\varphi) \cdot k_\varphi, \quad (8)$$

where k_l (expression is given above) and $k_\varphi = (1/\varphi_0)(d\varphi/dP)$ are pressure coefficients of compressibility of average Mn-O bond lengths and Mn-O-Mn bond angles, respectively. The pressure dependences of Mn-O bond length (a) and Mn-O-Mn bond angle (b) in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ constructed based on structural data from references Kozlenko *et al.* (2004) and Kozlenko and Savenko (2006) are shown in Fig. 16. It can be seen that the Mn-O bond length linearly decreases with $k_l \approx 0.0020 \text{ GPa}^{-1}$, while the Mn-O-Mn bond angle slightly increases with $k_\varphi = 0.0010 \text{ GPa}^{-1}$ in the pressure range of 0–8 GPa (Kozlenko *et al.*, 2004; Kozlenko and Savenko, 2006). Using the experimental structural values, the estimated value of dT_C/dP is 3.1 K/GPa, close to the experimental one, meaning that the pressure behavior of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ can be explained in terms of the modification of structural parameters only (Kozlenko *et al.*, 2004; Kozlenko and Savenko, 2006).

On the other hand, for the FM phase in orthorhombic manganites $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$, $\text{Pr}_{1-x}\text{Ba}_x\text{MnO}_3$, $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x \sim 0.3$, application of pressure suppresses the FM phase and stabilizes the layered A-type AFM phase around $P \sim 2 \text{ GPa}$. One of the important factors responsible for the difference between the properties of the manganites with the rhombohedral and orthorhombic crystal structure is the relevant symmetry of MnO_6 octahedra. The isotropic compression of the oxygen octahedra in the rhombohedral structure may be responsible for the stability of the FM phase, while the anisotropic uniaxial compression of the oxygen octahedra along the b axis in the $Pnma$ orthorhombic structure, mediating polarization of the $d_{x^2-z^2}$ e_g orbitals, is the origin of the occurrence of the A-type AFM phase at high pressure.

Fig. 17 represents the pressure dependence of Mn-O1 and $\langle \text{Mn-O2} \rangle$ mean bond lengths in the orthorhombic crystal structure of $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ constructed based on data from references Kozlenko *et al.* (2006, 2013). The compressibility of the Mn-O1 bond along the b axis significantly exceeds the average compressibility of Mn-O2 bonds in the (ac) planes. In the case of such a pseudo-tetragonal distortion of MnO_6 oxygen octahedra, ($t = (\text{Mn-O1})/\langle \text{Mn-O2} \rangle < 1$), a preferential polarization of the $d_{x^2-z^2}$ orbitals is expected, which consequently results in a weakening of the FM double exchange along the b -axis and the AFM superexchange becomes dominant interaction in this direction. These factors ensure favorable conditions for the formation of the A-type AFM state (Kozlenko *et al.*, 2013).

Moreover, from the pressure dependence of Curie temperature T_C of $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ constructed based on data from references Kozlenko *et al.* (2005, 2006, 2013); Kozlenko and Savenko (2006) and Dang *et al.* (2013) (Fig. 18), it can be seen that the pressure coefficient dT_C/dP of the FM phase in $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is 2.3 K/GPa, which is much smaller than $dT_C/dP \sim 12 \text{ K/GPa}$ observed for $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ having a smaller tolerance factor. The value dT_C/dP of $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is close to that of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, indicating an insignificant contribution of the electron-phonon interaction associated with the static cooperative Jahn–Teller distortion of oxygen octahedra to the physical properties of $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. On the other hand, in the case of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ the pressure-induced variation of the structural parameters contributes just 15% to the experimental value of dT_C/dP , indicating an important role of the electron-phonon interaction. Indeed, the polaron binding energy $E_{JT} \approx 200 \text{ meV}$ for $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ is significantly larger compared to $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (Kozlenko and Savenko, 2006). Furthermore, the variation of E_{JT} and the frequency of the phonon oscillation mode of oxygen octahedra $\hbar\omega$ upon compression can be estimated from electrical resistance and Raman scattering data, respectively (Kozlenko and Savenko, 2006). As pressure increases up to 5 GPa, E_{JT} decreases from 200 to 150 meV, while the mode frequency $\hbar\omega$ increases from 78 to 82 meV. In accordance to the Eq. (6) and assuming that $\gamma = 1$, the calculated value $(dT_C/dP)_{\text{calc}}$ is 16 K/GPa, consistent with the experimental one. For more accurately estimating the value of $(dT_C/dP)_{\text{calc}}$ the pressure behavior of γ should be considered.

Similarly, the pressure-induced FM to A-type AFM magnetic phase transition has also occurred in tetragonal $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ compounds with $x \sim 0.5$ (Kozlenko and Savenko, 2006). Furthermore, for $\text{Pr}_{0.44}\text{Sr}_{0.56}\text{MnO}_3$ system with Sr concentration value in vicinity to the A-type and C-type AFM boundary a magnetic phase transition from the A-type orthorhombic AFM structure ($T_N = 215 \text{ K}$) to the C-type tetragonal AFM one ($T_N = 125 \text{ K}$) occurs at $P \sim 2 \text{ GPa}$ (Kozlenko and Savenko, 2006). With further increasing pressure to 4.8 GPa, the A-type AFM phase is gradually suppressed at the expense of the C-type AFM one. At last, the C-type and G-type AFM phases are stable under pressures up to 5 GPa as observed in $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x > 0.8$) (Kozlenko and Savenko, 2006; Kozlenko *et al.*, 2010).

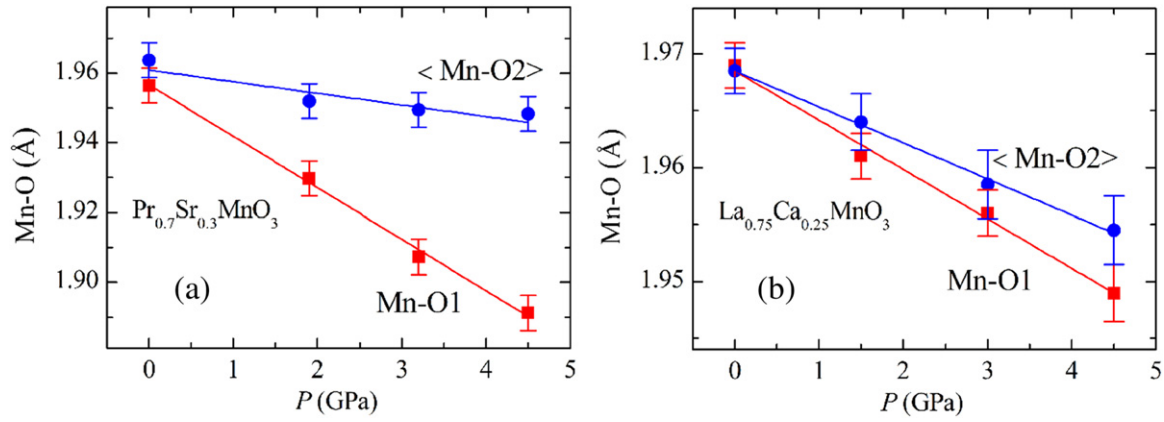


Fig. 17 Pressure dependence of Mn-O1 and <Mn-O2> mean bond lengths in the orthorhombic crystal structure of $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (a) and $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ (b).

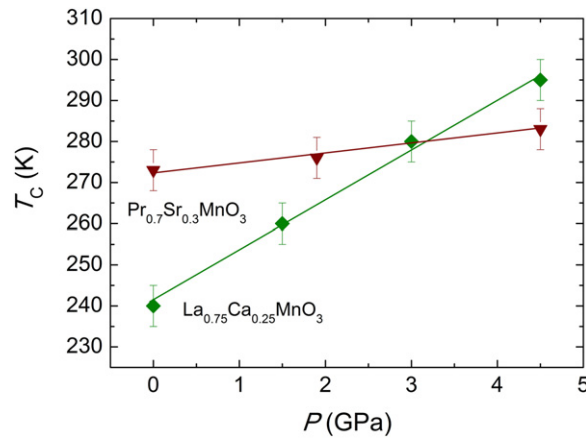


Fig. 18 Pressure dependence of Curie temperature T_C of $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$.

In the case of manganites with a smaller average (R_A) ion radius, a pressure-induced suppression of the insulating CE-type AFM ground state is in favor of the metallic A-type AFM state, which was observed in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ at $P \sim 3.5$ GPa (Cui *et al.*, 2003; Yu *et al.*, 2005). At the same time, neutron diffraction studies have shown a pressure-induced enhancement of the CE-type AFM state in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with the pressure coefficient $dT_N/dP = 4$ K/GPa under compression of 6 GPa (Kozlenko *et al.*, 2007). The existence of a pronounced electron-phonon coupling and charge localization is the origin of the stability of the CE-type AFM phase under pressures in compounds with small enough $r_{(R,A)}$ and bandwidth such as $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, and properly $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.

The aforementioned pressure-induced magnetic phase transitions in $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ manganites can be explained in terms of the simple degenerate DE model, which considers the interplay between the superexchange AFM interaction J_{AF} and the FM double exchange controlled by the p - d electron transfer integral b_{p-d} with the Hund's coupling $J_H > b_{p-d}$ (Venkateswara Pai, 2001). Since the parameters J_{AF} and b_{p-d} differently depend on the Mn-O bond length d ($J_{AF} \sim d^{-14}$ and $b_{p-d} \sim d^{-3.5}$), the superexchange strength will be enhanced more progressively and overcome double exchange one under pressure, resulting in an increase of the parameter $J_{AF}S^2/b_{p-d} \sim d^{-10.5}$ (S is the Mn^{3+} spin value) (Kozlenko and Savenko, 2004, 2006). The theoretical calculations (Venkateswara Pai, 2001) show that increase in the $J_{AF}S^2/b_{p-d}$ parameter induces the sequence of the FM $\rightarrow$ A-type AFM $\rightarrow$ C-type AFM transitions in manganites with $x \sim 0.5$ and C-type AFM $\rightarrow$ G-type AFM in manganites with $x > 0.8$.

Conclusions

In this article, we have provided important insights into the physics of perovskite transition-metal oxides, with a special emphasis on manganites that exhibit fascinating and exotic physical properties. The general features of structural behaviors in these materials are outlined. The evolution of crystal and magnetic structures of manganites as functions of chemical composition, temperature, or pressure has been discussed in detail, based mostly on the neutron diffraction data analysis. A rich variety of physical phenomena

observed in manganites, including the colossal magnetoresistance, insulator-metal transitions, charge and orbital ordering, generous magnetic phase transitions, multiferroic behavior, is driven by a complex interplay of competing magnetic interactions, electron phonon coupling, structural distortions and charge localization effects, controlled by variation of structural parameters. The analyzed relationships among the features of the crystal structure and response of magnetic and associated physical properties provide an important background of knowledge for further development of advanced oxide materials with enhanced functionality and tunability.

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Advanced Magnetic Microwires for Sensing Applications

Arcady P Zhukov, Department Advanced Polymers and Materials: Physics, Chemistry and Technology, Faculty of Chemistry, UPV/EHU and Department of Applied Physics, EIG, UPV/EHU, San Sebastian, Spain and IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

Mihail Ipatov, Department Advanced Polymers and Materials: Physics, Chemistry and Technology, Faculty of Chemistry, UPV/EHU, San Sebastian, Spain

Paula Corte-Leon, Department Advanced Polymers and Materials: Physics, Chemistry and Technology, Faculty of Chemistry, UPV/EHU, and Department of Applied Physics, EIG, UPV/EHU, San Sebastian, Spain

Juan M Blanco, Department of Applied Physics, EIG, UPV/EHU, San Sebastian, Spain

Valentina Zhukova, Department Advanced Polymers and Materials: Physics, Chemistry and Technology, Faculty of Chemistry, UPV/EHU, and Department of Applied Physics, EIG, UPV/EHU, San Sebastian, Spain

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Abstract

Several routes allowing the development of low cost magnetic microwires coated by flexible, insulating and biocompatible glass-coating with tunable magnetic properties are overviewed. Amorphous microwires present excellent soft magnetic properties and the giant magnetoimpedance (GMI) effect. The GMI effect, obtained even in as-prepared Co-rich microwires, can be further improved by appropriate annealing (including conventional annealing, stress-annealing, and Joule heating). While as-prepared Fe-rich microwires often exhibit low GMI effect, magnetic softening and GMI effect improvement can be achieved in Finemet-type microwires upon nanocrystallization. Stress-annealing and combined stress-annealed followed by conventional annealing also yield remarkable (more than an order of magnitude) GMI improvement in amorphous Fe-rich microwires.

Introduction

Sensors provide the ability to detect and track events or changes in the environment using electronic devices, such as a computer processor, and therefore play a critical role in most modern industries (i.e., microelectronics, automotive, aerospace and aviation, security and electronic surveillance, home entertainment, computer science, medicine, construction, electrical engineering, etc.) (Wilson *et al.*, 2007; Lenz and Edelstein, 2006; Rivero *et al.*, 2012).

Magnetic sensors have assisted in monitoring, analysis and control of various processes and functions for many decades.

Depending on the type of events or environmental changes, different types of magnetic sensors can be used; for example, sensors that allow detecting weak magnetic fields or small changes in the magnetic field, sensors that are sensitive to other external stimuli such as mechanical stress, mechanical vibrations, temperature, etc., (Wilson *et al.*, 2007; Lenz and Edelstein, 2006; Rivero *et al.*, 2012; Díaz-Michelena, 2009; Mohri *et al.*, 2015; Ma *et al.*, 2019; Karsenty, 2020; Zheng *et al.*, 2019). Accordingly, completely different phenomena can be used for different types of magnetic sensors. Among the phenomena suitable for detection and measurements of a magnetic field, Hall effect, anisotropic magnetoresistance (AMR), Giant magnetoresistance (GMR), tunneling magnetoresistance (TMR), and Giant magnetoimpedance (GMI) are widely known (Mohri *et al.*, 2015; Zheng *et al.*, 2019; Baibich *et al.*, 1988; Inoue and Maekawa, 1996). Magnetostrictive materials, stress-impedance, microwave composite materials and flexible electronics are suitable for stresses and vibrations detections (Blanco *et al.*, 1999; Makhnovskiy *et al.*, 2008; Karnaushenko *et al.*, 2015). Most of such effects are summarized in Table 1.

As a rule, the use of magnetic sensors is limited by their cost, environmental conditions and relatively weak magnetic signals (Rivero *et al.*, 2012; Díaz-Michelena, 2009; Mohri *et al.*, 2015; Ma *et al.*, 2019). Accordingly, the main trends in the magnetic sensors are the development of cost effective, fast, precise, sensitive and effective sensing technologies and methods.

To a great extend, the sensors performance is determined by the properties of the material from which a given type of magnetic sensor is made.

Considerable attention is paid to the use of nanomaterials or nanotechnologies (magnetic nanostructures, multilayered nanomaterials, thin-films, nanotags,) for magnetic sensors development (Wilson *et al.*, 2007; Zheng *et al.*, 2019; Coisson *et al.*, 2012). The main advantage of thin films and laminates is that they are compatible with integrated electronic devices and can present several of the properties mentioned in Table 1, like GMR, AMR or TMR (Baibich *et al.*, 1988; Inoue and Maekawa, 1996). However, nanostructured materials are not universal materials for magnetic sensors and devices design. For example, nanostructures prepared using sputtering, evaporation, ablation or deposition methods, such as thin films, generally present much poorer magnetic softness (and hence the lower GMI effect) (Coisson *et al.*, 2012).

For a rather wide family of magnetic sensors, however, soft magnetic materials are of fundamental importance (Mohri *et al.*, 2015; Ma *et al.*, 2019; Fiorillo *et al.*, 1999; Zhukov, 2017a, 2020a).

Amorphous magnetic materials often possess excellent soft magnetic properties together with good mechanical properties (Zhukov, 2017a, 2020a; Herzer, 1997; Hagiwara *et al.*, 1982; Rudkowski *et al.*, 1991; Goto *et al.*, 1977; Zhukova *et al.*, 2002a). In most cases, good magnetic softness can be obtained in as-prepared amorphous materials without sophisticated post-processing usually required for crystalline magnetic materials (Fiorillo *et al.*, 1999; Zhukov, 2017a). In most crystalline magnetic materials,

Table 1 Different types of technologies used for detection of different types of external stimuli

<i>Magnetic field</i>	<i>Stresses, vibrations</i>	<i>Position</i>	<i>Heating, temperature</i>
Hall effect	Stress-impedance	Magnetoimpedance	Hyperthermia
Magnetoresistance effects (AMR, GMR, TMR)	Magnetostrictive materials	Magnetic shape memory	Composite with magnetic inclusions
Fluxgate	Flexible electronics		Magnetoimpedance
Magnetoimpedance	Composite with magnetic inclusions		
SQUID	Magnetic bistability		
Search coils			

magnetic softness is essentially limited by defects, like grain boundaries, dislocations, texture, etc. Additionally, the fabrication technique, involving rapid melt quenching, is a rather fast and inexpensive fabrication method (Zhukov, 2017a; Herzer, 1997; Hagiwara *et al.*, 1982; Rudkowski *et al.*, 1991). In addition, the rapid quenching technique can be used for the fabrication of granular materials that can present the GMR effect (Chien *et al.*, 1993; Zhukova *et al.*, 2012).

Generally, amorphous materials can be prepared in planar (ribbons) or cylindrical (wires) forms.

Amorphous ribbons have been proposed and explored for several applications, like transformers, magnetic shields, acoustic delay lines, tensile stress transducers and transverse filters, inductive components for switched mode power supplies, magnetic heads for data storage applications (McHenry *et al.*, 1999; Luborsky, 1985).

However, for several phenomena, like the GMI effect or magnetic bistability, the cylindrical shape is more favorable.

Indeed, the origin of the GMI effect has been satisfactorily explained in terms of the skin effect, i.e., dependence of the skin depth, δ , on applied magnetic field, H , in materials with high magnetic permeability (Mohri *et al.*, 2002; Panina and Mohri, 1994; Beach and Berkowitz, 1994; Knobel *et al.*, 2003; Zhukov *et al.*, 2015a,b,c; Phan and Peng, 2008). As a rule, the highest GMI effect is observed in Co-rich magnetic wires with high circumferential magnetic permeability, μ_ϕ (Pirota *et al.*, 2000; Corte-León *et al.*, 2019a,b). For the case of a soft magnetic wire, $\delta(\mu_\phi)$ dependence is expressed as (Panina and Mohri, 1994; Beach and Berkowitz, 1994):

$$\delta = 1 / \sqrt{\pi \sigma \mu_\phi f} \quad (1)$$

where σ is the electrical conductivity and f is the AC current frequency. Accordingly, high μ_ϕ -values are a prerequisite for achieving a high GMI effect (Panina and Mohri, 1994; Beach and Berkowitz, 1994; Knobel *et al.*, 2003; Zhukov *et al.*, 2015a,b,c; Phan and Peng, 2008).

On the other hand, amorphous wires can present perfectly rectangular hysteresis loops originated by fast magnetization switching through a single and large Barkhausen jump between two remanent states with opposite magnetization (Mohri *et al.*, 1990; Vazquez and Chen, 1995; Aragonese *et al.*, 1998). In such magnetic wires, the demagnetized state cannot be observed, and the magnetization reversal occurs by fast domain wall propagation (Ogasawara and Ueno, 1995; Vazquez and Chen, 1995; Zhukova *et al.*, 2020a,b,c,d).

Accordingly, magnetic wires have been proposed for several magnetic sensor applications, like magnetic field sensors, magnetoelastic sensors, magnetic memory and logics (Cobeño *et al.*, 2001; Ding *et al.*, 2009; Ma *et al.*, 2019; Makhnovskiy *et al.*, 2008, 2011; Mohri *et al.*, 2002, 2015; Uchiyama *et al.*, 2011).

Amorphous wires with wide diameters, d , range can be prepared by a variety of rapid melt quenching techniques:

- (1) The so-called “in-rotating water” method allows preparation of amorphous wires with $60 \leq d \leq 320 \mu\text{m}$ (Hagiwara *et al.*, 1982; Ogasawara and Ueno, 1995).
- (2) The so-called melt extraction technique is suitable for fabrication of amorphous wires with $30 \leq d \leq 60 \mu\text{m}$ (Rudkowski *et al.*, 1991; Zhukova *et al.*, 2003a; Liu *et al.*, 2012).
- (3) Glass-coated (composite) microwires with metallic nucleus diameters, d , from 185 nm (Ovári *et al.*, 2012) up to 100 μm (Corte-León *et al.*, 2020a) can be obtained by so-called modified Taylor-Ulitovsky (also known as quenching-and-drawing) method known since the 60-s (Goto *et al.*, 1977; Ulitovsky *et al.*, 1960; Kraus *et al.*, 1976).

The latter method allows varying the diameter of the metallic nucleus of a glass-coated microwire by almost 3 orders of magnitude and preparing the thinnest and up to 10 km long amorphous rapidly quenched wires. Additionally, magnetic microwires prepared using the Taylor-Ulitovsky method are covered by a thin flexible and biocompatible glass coating that allows anti-corrosive and mechanical properties improvement and the biocompatibility (Goto *et al.*, 1977; Kozejova *et al.*, 2019; Mitxelena-Iribarren *et al.*, 2020).

One of the latest trends in the field of amorphous materials is the development of rapidly quenched amorphous materials with reduced dimensionality and biocompatibility. These features are desirable for inclusion in the field of biomedicine applications, as well as in magnetic memories and magnetic logic devices (Kozejova *et al.*, 2019; Mitxelena-Iribarren *et al.*, 2020; Parkin *et al.*, 2008; Allwood *et al.*, 2005). Accordingly, the development of low dimensional, inexpensive and robust soft magnetic materials has attracted growing attention.

Glass-coated microwires are such materials that meet several requirements, such as reduced dimensionality, excellent magnetic softness, biocompatibility, excellent mechanical and anti-corrosion properties (Makhnovskiy *et al.*, 2008; Zhukova *et al.*, 2002a, 2012a; Kozejova *et al.*, 2019; Pirota *et al.*, 2000; Corte-León *et al.*, 2019a,b). Given the excellent combination of physical properties (magnetic, mechanical, corrosive) and a fast and inexpensive manufacturing method, glass-coated microwires are potentially suitable materials for many industrial applications.

Applications involving the GMI effect are mainly related to the high sensitivity of electrical impedance to magnetic field or stress and include electronic compass for smartphones and wristwatches, biomagnetic field sensing, human magnetocardiogram and magnetoencephalogram, nonvolatile magnetic memory, magnetoelastic sensors, magnetometers, smart composites and metamaterials (Allue *et al.*, 2019; Ding *et al.*, 2009; Ipatov *et al.*, 2016; Makhnovskiy *et al.*, 2008; Mohri *et al.*, 2015; Nabias *et al.*, 2018; Qin and Peng, 2013). On the other hand, magnetic bistability and associated domain wall (DW) propagation are suggested for electronic surveillance, torque sensors, noncontact mechanocardiograph, racetrack memories, magnetic logics, etc., (Mohri *et al.*, 2002; Panina and Mohri, 1994; Beach and Berkowitz, 1994; Mohri *et al.*, 1990; Makhnovskiy *et al.*, 2011; Parkin *et al.*, 2008; Allwood *et al.*, 2005; Zhukova *et al.*, 2021).

Accordingly, in this article, we provide an overview of the routes to optimize the magnetic and magnetotransport properties of glass-coated magnetic microwires suitable for magnetic sensor applications.

Background/Fundamentals

In this article, we will deal with the optimization of magnetic softness and GMI effect, as well as tuning of switching field in magnetically bistable microwires. Provided below is the essential background information on both phenomena.

The GMI effect consists of a large change in the electrical impedance under the action of an applied magnetic field (Zhukov *et al.*, 2020a; Panina and Mohri, 1994; Beach and Berkowitz, 1994; Knobel *et al.*, 2003; Zhukov *et al.*, 2015a; Phan and Peng, 2008).

The main features of the GMI effect are the followings:

1. The total impedance change of at least 100%. The most commonly used expression for the GMI effect is the GMI ratio, $\Delta Z/Z$, defined as (Panina and Mohri, 1994; Beach and Berkowitz, 1994; Knobel *et al.*, 2003; Zhukov *et al.*, 2015a; Phan and Peng, 2008):

$$\Delta Z/Z = [Z(H) - Z(H_{\max})]/Z(H_{\max}) \times 100 \quad (2)$$

where $H_{\max}$ is the maximum axial DC magnetic field (usually up to few kA/m).

Experimentally, the highest $\Delta Z/Z$ - values (up to 650%) have been reported for amorphous wires with high circumferential permeability (Zhukov *et al.*, 2020a; Pirota *et al.*, 2000; Corte-León *et al.*, 2019a,b). Although $\Delta Z/Z \approx 600\%$ has been reported even in as-prepared magnetic microwires with magnetic anisotropy tuned through the geometry of amorphous microwires (Zhukov *et al.*, 2005), such high $\Delta Z/Z$ - values are often achieved after appropriate post-processing (Pirota *et al.*, 2000; Corte-León *et al.*, 2019a,b).

2. Good magnetic softness is directly related to the GMI effect: wires, ribbons or films with high $\Delta Z/Z$ - values are usually extremely soft magnetic materials (Zhukov *et al.*, 2020a; Pirota *et al.*, 2000; Panina and Mohri, 1994; Beach and Berkowitz, 1994; Knobel *et al.*, 2003; Zhukov *et al.*, 2015a; Phan and Peng, 2008; Corte-León *et al.*, 2019a,b). Additionally, the magnetic field dependence of the GMI ratio, $\Delta Z/Z(H)$ is determined by the type of magnetic anisotropy. Thus, the circumferential anisotropy leads to the observation of the maximum of the real component of wire impedance, Z , versus H (and, consequently, in the $\Delta Z/Z(H)$). However, in the case of axial magnetic anisotropy, the maximum value of the GMI ratio corresponds to $H = 0$ (Usov *et al.*, 1998), i.e., which results in a monotonic decay of the GMI ratio with the axial magnetic field.
3. The theoretically predicted maximum GMI ratio is about 3000% (Kraus, 1999). Additionally, the theoretically estimated skin depth minimum is about $0.3 \mu\text{m}$ (Kraus, 1999; Ipatov *et al.*, 2010). Correspondingly, for achievement of this substantial GMI ratio, the sample diameter must be at least an order of magnitude higher, i.e., above $3 \mu\text{m}$. Therefore, soft magnetic materials with micrometric dimensionality (wire diameters or ribbon thickness of the order of $3\text{--}30 \mu\text{m}$) are almost ideal materials for realization of such high $\Delta Z/Z$ - values.
4. The AC current plays an important part in the GMI effect. The main reason is that like magnetic permeability, GMI effect presents tensor character (Usov *et al.*, 1998; Aragonese *et al.*, 2000). Therefore, AC current flowing through the sample creates circumferential magnetic field. Additionally, AC current can produce the Joule heating (Aragonese *et al.*, 2000; Zhukova *et al.*, 2018a). Therefore, the AC current amplitude must be carefully selected.
5. The AC current frequency f as well as the comparison of the skin depth with the radius or half thickness of the sample is one more relevant parameter: depending on f four different GMI regimes might be considered. At low f range (typically $1\text{--}10 \text{ kHz}$) the skin depth, δ , is typically larger than the radius or half thickness of the sample (rather weak skin effect) the Matteucci effect and magnetoinductive effect have been observed (Zhukov, 1993; Cobeño *et al.*, 1999; Mohri *et al.*, 1993). The impedance changes in this regime are due to a circular magnetization process exclusively (Cobeño *et al.*, 1999). Therefore, considering that the origin of GMI effect is associated with the skin effect of magnetic conductor, observed phenomena might not be considered properly as the GMI effect. In the f range from 10 to 100 kHz to $1\text{--}10 \text{ MHz}$, the GMI effect originates from variations in Δ caused by strong changes in the effective magnetic permeability, μ , caused by a DC magnetic field (Zhukov *et al.*, 2020a; Panina and Mohri, 1994; Beach and Berkowitz, 1994; Knobel *et al.*, 2003; Zhukov *et al.*, 2015a; Phan and Peng, 2008). It is widely believed that in this case both the DWs and the magnetization rotation contribute to a change in μ and, consequently, to the skin effect. For MHz f band (from 1 to 10 MHz to $100\text{--}1000 \text{ MHz}$ depending on the geometry of the sample), the GMI effect is also originated by the skin effect of the soft magnetic conductor, although the DWs are strongly damped. Therefore, the magnetization rotation must be considered as responsible for the magnetic permeability change induced by an external magnetic field (Zhukov *et al.*, 2020a; Knobel *et al.*, 2003; Zhukov *et al.*, 2015a; Phan and Peng, 2008; Ménard *et al.*, 1998).

Finally, in GHz f range the magnetization rotation is strongly influenced by the gyromagnetic effect. With f increasing, the GMI peaks are shifted into DC fields, where the sample is magnetically saturated. In this f range, strong changes of the sample impedance have been linked to the ferromagnetic resonance (FMR) (Ménard *et al.*, 1998; Zhukov *et al.*, 2020a; Zhukov *et al.*, 2015a; Phan and Peng, 2008). We must emphasize that the criterion used the f ranges definition is somewhat artificial. Probably, the most suitable criteria is the ratio of the skin depth, δ , to the transverse sample dimension, a , δ/a , used by several authors (Ménard *et al.*, 1998; Zhukov *et al.*, 2020a; Phan and Peng, 2008; Ipatov *et al.*, 2008). In this case, the appropriate criteria should be the ratio δ/a : $\delta/a \gg 1$ indicates a weak skin effect regime, while $\delta/a \ll 1$ indicates a strong skin effect. However, δ/a ratio depends on several parameters, such as sample dimensions, material properties, magnetic field, etc. Therefore, this criterion also does not seem to be appropriate for the distinction among different frequency ranges. The other important parameter is the DWs contribution: whether they damped or not.

Phenomenologically the GMI effect consists of the change of the AC impedance, $Z = R + iX$ (where R is the real part, or resistance, and X is the imaginary part, or reactance), upon an external magnetic field, H .

The electrical impedance, Z , of a magnetic conductor is given by Panina and Mohri (1994); Beach and Berkowitz (1994):

$$Z = R_{dc}krJ_0(kr)/2J_1(kr) \quad (3)$$

where R_{dc} is the electrical resistance for a DC current, $k = (1 + j)/\delta$, J_0 and J_1 are the Bessel functions, r is the wire radius and δ is given by Eq. (1).

It is worth noting the magnetic permeability and hence the impedance possess tensor nature in ferromagnetic materials (Usov *et al.*, 1998; Aragonese *et al.*, 2000; Sandacci *et al.*, 2004; Knobel *et al.*, 2003; Zhukov *et al.*, 2015a; Phan and Peng, 2008). The excitation and measurement methods revealing the impedance matrix elements are described elsewhere (Zhukov *et al.*, 2020b; Sandacci *et al.*, 2004; Zhukov *et al.*, 2008).

The use of specially designed micro-strip sample holder and the evaluation of the sample impedance from the reflection coefficient S_{11} using the vector network analyzer allow for measurements of the GMI effect up to GHz frequencies (Zhukov *et al.*, 2012c; Zhukov *et al.*, 2020b).

As mentioned above, amorphous magnetic wires can present spontaneous magnetic bistability originated by a single and large Barkhausen jump between two remanent states with opposite magnetization. In such magnetically bistable wires the magnetization switching runs by fast DW propagation. As experimentally observed elsewhere (Vazquez and Chen, 1995; Zhukova *et al.*, 2020a), such DW propagation starts from the microwire ends, where the closure domains exist because of the demagnetizing field effect.

Development of Magnetic Microwires With Optimized Magnetic Properties

Magnetic Properties of As-Prepared Magnetic Microwires: Effect of Chemical Composition and Magnetoelastic Anisotropy

Perfectly cylindrical geometry of magnetic microwires prepared using the Taylor-Ulitovsky technique is suitable for realization of either the Giant Magnetoimpedance (GMI) effect (Knobel *et al.*, 2003; Zhukov *et al.*, 2015a; Phan and Peng, 2008; Pirota *et al.*, 2000; Corte-León *et al.*, 2019a,b) or magnetic bistability associated with fast magnetization switching by ultrafast domain wall propagation (Mohri *et al.*, 1990; Vazquez and Chen, 1995; Zhukova *et al.*, 2020a; Corte-León *et al.*, 2020b; Zhukova *et al.*, 2021).

As known from previous experimental studies, the character of hysteresis loops of as-prepared amorphous microwires is affected by the magnetostriction coefficient, λ_s , linked to the chemical composition of the metallic alloys (Herzer, 1997; Mohri *et al.*, 1990; Zhukov *et al.*, 2017b; Corte-León *et al.*, 2020b; Zhukov *et al.*, 2012b). Typically, in $\text{Co}_x\text{Fe}_{1-x}$ and $\text{Ni}_x\text{Fe}_{1-x}$ based amorphous alloys ($0 \leq x \leq 1$) the λ_s -values changes from high and positive λ_s -values ($\lambda_s \approx 35\text{--}40 = 10 \times 10^{-6}$) for $x = 0$ (i.e., for the Fe-based alloys) to negative λ_s -values (typically $\lambda_s \approx -5 \times 10^{-6}$) for $x = 1$ (Co-rich amorphous alloys) (Herzer, 1997; Churyukanova *et al.*, 2016). Ni-rich amorphous alloys present low saturation magnetization and Curie temperature. Therefore, vanishing or negative λ_s -values can be obtained only in Co-rich amorphous alloys (Herzer, 1997).

Accordingly, the hysteresis loops character is primary affected by the λ_s sign.

In this article, we will analyze Fe-,Co-Ni- based microwires. The chemical composition, geometry, and magnetostriction coefficient of the analyzed microwires are provided in Table 2.

As observed from Fig. 1, Fe-rich $\text{Co}_x\text{Fe}_{1-x}$, $\text{Co}_x\text{Ni}_y\text{Fe}_{1-x-y}$ and $\text{Ni}_x\text{Fe}_{1-x}$ based as-prepared amorphous microwires with positive λ_s -values typically present perfectly rectangular hysteresis loops (see Fig. 1(a-c)). In contrast, Co-rich microwires (either with $\lambda_s \approx 0$ or $\lambda_s < 0$) typically present linear almost unhysteretic magnetization curves with low coercivities, H_c (see Fig. 1(d,e)).

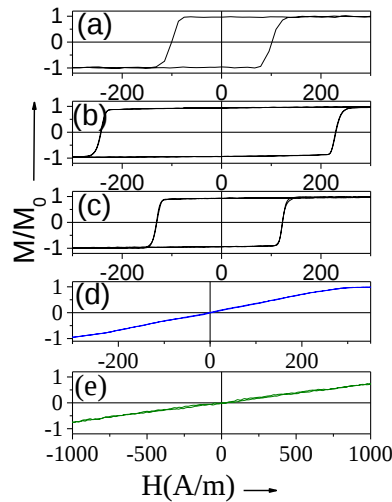
Such influence of the λ_s sign and value is commonly discussed in terms of the magnetoelastic anisotropy, which plays a decisive role in tuning the magnetic anisotropy of amorphous materials.

However, λ_s is not the unique factor that affects the magnetoelastic anisotropy constant, K_{me} : another relevant parameter is the stress value, σ , given as $\sigma = \sigma_i + \sigma_{app}$ where σ_i and σ_{app} are the internal and applied stresses, respectively. Accordingly, K_{me} is given by (Zhukov *et al.*, 2013; Chiriac *et al.*, 2007; Zhukova *et al.*, 2020b; Astefanoaei *et al.*, 2006; Chiriac *et al.*, 2003; Aronin *et al.*, 2013):

$$K_{me} \approx 3/2\lambda_s\sigma \quad (4)$$

Table 2 Composition, geometry, and magnetostriction coefficient of the studied glass-coated microwires

Composition	Metallic nucleus diameter, d (μm)	Total diameter, D (μm)	Ratio $\rho = d/D$	Magnetostriction coefficient, $\lambda_s \times 10^{-6}$
$\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$	15.2	17.2	0.88	38
$\text{Fe}_{70}\text{B}_{15}\text{Si}_{10}\text{C}_5$	15	23.8	0.63	38
$\text{Fe}_{70}\text{B}_{15}\text{Si}_{10}\text{C}_5$	10.8	22.5	0.48	38
$\text{Fe}_{70}\text{B}_{15}\text{Si}_{10}\text{C}_5$	6	23.1	0.26	38
$\text{Fe}_{70}\text{B}_{15}\text{Si}_{10}\text{C}_5$	3	18.8	0.16	38
$\text{Fe}_{77.5}\text{Si}_{7.5}\text{B}_{15}$	15.1	35.8	0.42	38
$\text{Fe}_{62}\text{Ni}_{15.5}\text{Si}_{7.5}\text{B}_{15}$	14.35	33.25	0.43	27
$\text{Fe}_{47.4}\text{Ni}_{26.6}\text{Si}_{11}\text{B}_{13}\text{C}_2$	29	32.2	0.9	20
$\text{Fe}_{16}\text{Co}_{60}\text{Si}_{13}\text{B}_{11}$	12	29	0.41	15
$\text{Co}_{77.5}\text{Si}_{15}\text{B}_{7.5}$	13.1	18	0.73	-5
$\text{Fe}_{36}\text{Co}_{40}\text{B}_{12.9}\text{Si}_{11.1}$	19.8	23.8	0.83	25
$\text{Co}_{67}\text{Fe}_{3.85}\text{Ni}_{1.45}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.7}$	6.6	15.7	0.42	-3
$\text{Co}_{67}\text{Fe}_{3.85}\text{Ni}_{1.45}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.7}$	9.8	18.5	0.53	-3
$\text{Co}_{67}\text{Fe}_{3.85}\text{Ni}_{1.45}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.7}$	16.8	24	0.7	-3
$\text{Co}_{67}\text{Fe}_{3.85}\text{Ni}_{1.45}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.7}$	16.8	21	0.8	-3
$\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$	22.8	23.2	0.98	-1
$\text{Co}_{67}\text{Fe}_{3.9}\text{Ni}_{1.5}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.6}$	25.6	26.6	0.96	-0.29
$\text{Fe}_{70.8}\text{Cu}_1\text{Nb}_{3.1}\text{Si}_{14.5}\text{B}_{10.6}$	5.8	15.2	0.38	30
$(\text{Fe}_{0.7}\text{Co}_{0.3})_{83.7}\text{Si}_4\text{B}_8\text{P}_{3.6}\text{Cu}_{0.7}$	22.3	26.5	0.84	
$\text{Fe}_{38.5}\text{Co}_{38.5}\text{B}_{18}\text{Mo}_4\text{Cu}_1$	10	16.6	0.6	

**Fig. 1** Hysteresis loops of amorphous magnetic microwires $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ ($\lambda_s > 0$) (a), $\text{Fe}_{36}\text{Co}_{40}\text{B}_{12.9}\text{Si}_{11.1}$ ($\lambda_s > 0$) (b), $\text{Fe}_{62}\text{Ni}_{15.5}\text{Si}_{7.5}\text{B}_{15}$ ($\lambda_s > 0$) (c), $\text{Co}_{67.1}\text{Fe}_{3.8}\text{Ni}_{1.4}\text{Si}_{14.5}\text{B}_{11.5}\text{Mo}_{1.7}$ ($\lambda_s \approx 0$, $\rho \approx 0.53$) (d) and $\text{Co}_{77.5}\text{Si}_{15}\text{B}_{7.5}$ ($\lambda_s < 0$) (e).

There are several sources of the internal stresses and factors affecting its spatial distribution: (1) the difference in the thermal expansion coefficients of the metallic alloy nucleus solidifying simultaneously with the glass coating surrounding it; (2) the quenching stresses related to the rapid solidification of the metallic alloy nucleus from the surface inside the wire axis; and (3) the drawing stresses (Chiriac *et al.*, 2007; Zhukova *et al.*, 2020b, 2012; Chiriac and Ovari, 2002; Baranov *et al.*, 2017).

Most theoretical estimations of the σ_i magnitude and its distribution indicate that the highest σ_i is a result of the difference in the thermal expansion coefficients of a metallic alloy and a glass coating (Chiriac *et al.*, 2007; Astefanoaei *et al.*, 2006).

These stresses are distributed in a complex way within the metallic nucleus. Thus, while radial stresses σ_r retain their sign being positive (tensile), axial stresses σ_{zz} and azimuthal stresses $\sigma_{\theta\theta}$ are positive (tensile) in the inner part of the metallic nucleus becoming negative (compressive) near the interface between metallic nucleus and glass-coating (Chiriac *et al.*, 2003; Zhukova *et al.*, 2020b). Thus, the radial distribution of the internal stresses is uneven: tensile stresses are strongest near the axis of the metal core. Axial internal stresses are the strongest and remain positive (tensile) in the main part of the metal core up to $0.85 d$. However, closer to the interface layer with the glass coating the compressive stresses are dominant (Chiriac *et al.*, 2003; Aronin *et al.*, 2013).

Several attempts to evaluate the quenching and drawing stresses have shown that they are roughly an order of magnitude lower (Chiriac *et al.*, 2007; Astefanoaei *et al.*, 2006).

In addition, the drawing stresses are of axial origin and, accordingly, they further increase the axial internal stresses arising from the difference in the thermal expansion coefficients of the metallic alloy and the glass coating (Astefanoaei *et al.*, 2006).

The internal stresses value inside the metallic nucleus can be tuned by the ρ -ratio between the metallic nucleus diameter, d , and the total microwire diameter, D ($\rho = d/D$). As predicted and experimentally confirmed, for a fixed glass-coating thickness, t_g , K_{me} decreases with an increase in d , whereas for a fixed d , K_{me} increases with an increase in t_g (Chiriac and Ovari, 2002; Chiriac *et al.*, 2003). Considering that $D = d + 2 t_g$, K_{me} decreases with ρ increasing.

Accordingly, even for the same metallic nucleus composition ($\text{Fe}_{70}\text{B}_{15}\text{Si}_{10}\text{C}_5$) H_c can be modified by almost an order of magnitude (from 85 to 630 A/m) by changing the ratio ρ (see Fig. 2). As can be seen from Fig. 2(e), H_c -values can be represented by $H_c(\rho)$ dependence.

For Co-rich microwires with $\lambda_s \approx 0$ ($\text{Co}_{67}\text{Fe}_{3.85}\text{Ni}_{1.45}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.7}$), the correlation of the hysteresis loops and the ρ -ratio is manifested by the change in the magnetic anisotropy field, H_k , (see Fig. 3(a-d)). If we plot H_k obtained from the hysteresis loops of $\text{Co}_{67}\text{Fe}_{3.85}\text{Ni}_{1.45}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.7}$ microwires with various d and D -values versus the ρ -ratio, we can find out that there is a correlation between H_k and ρ -ratio. Magnetic anisotropy field, H_k , increases with the decrease in ρ -ratio (Fig. 3(e)). All the samples with different ρ -ratios present linear almost non-hysteretic loops with low H_c -values (up to 4 A/m).

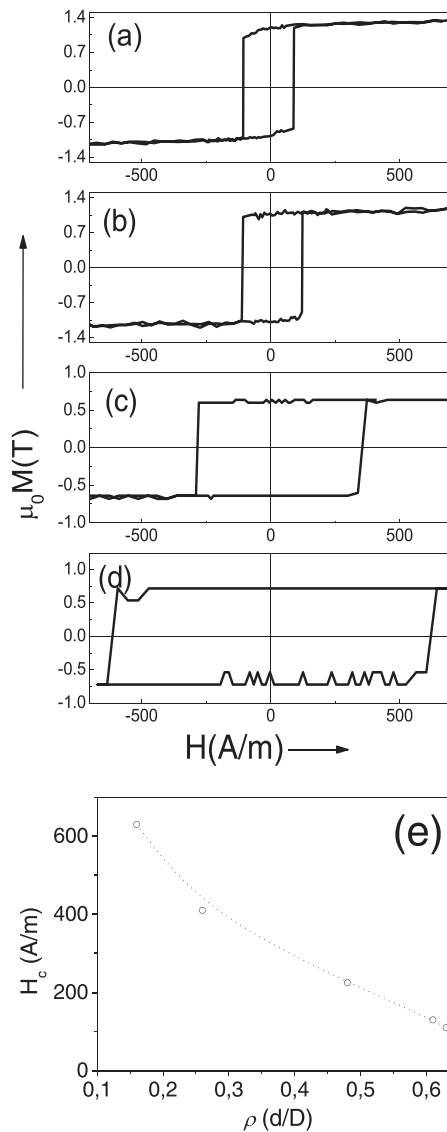


Fig. 2 Hysteresis loops of $\text{Fe}_{70}\text{B}_{15}\text{Si}_{10}\text{C}_5$ amorphous microwires with different metallic nucleus diameter d and total diameters D : with $\rho = 0.63$; $d = 15 \mu\text{m}$ (a); $\rho = 0.48$; $d = 10.8 \mu\text{m}$ (b); $\rho = 0.26$; $d = 6 \mu\text{m}$ (c); $\rho = 0.16$; $d = 3 \mu\text{m}$ (d) and $H_c(\rho)$ dependence (e) of the same microwires. Reprinted from Zhukova, V., Corte-Leon, P., González-Legarreta, L., *et al.*, 2020b. Optimization of magnetic properties of magnetic microwires by post-processing. Processes 8, 1006. Available at: <https://doi.org/10.3390/pr8081006>.

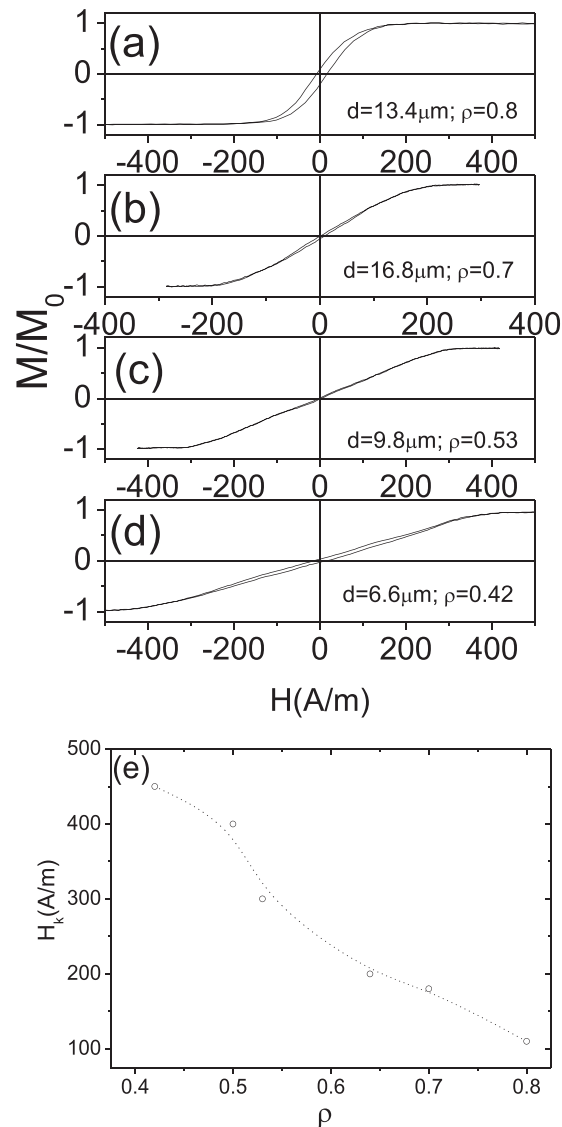


Fig. 3 Hysteresis loops of $\text{Co}_{67.1}\text{Fe}_{3.8}\text{Ni}_{1.4}\text{Si}_{14.5}\text{B}_{11.5}\text{Mo}_{1.7}$ microwires with different geometry (a-d) and $H_k(\rho)$ dependence for the same microwires (e). Adapted from Zhukova, V., Corte-Leon, P., González-Legarreta, L., *et al.*, 2020b. Optimization of magnetic properties of magnetic microwires by post-processing. Processes 8, 1006. Available at: <https://doi.org/10.3390/pr8081006>.

Accordingly, from the character of hysteresis loops of magnetic microwires with positive λ_s , magnetization reversal can be expected due to DW propagation, and therefore such microwires are potentially suitable for applications involving magnetic bistability and DW propagation.

Obviously, magnetization reversal of Co-rich microwires with linear hysteresis loops runs by the magnetization rotation and hence DW propagation cannot be observed. However, such Co-rich microwires present the higher GMI effect as evidenced from Fig. 4.

As-compared to $\text{Co}_{67.1}\text{Fe}_{3.8}\text{Ni}_{1.4}\text{Si}_{14.5}\text{B}_{11.5}\text{Mo}_{1.7}$ ($\lambda_s \approx 0$), and $\text{Co}_{77.5}\text{Si}_{15}\text{B}_{7.5}$ ($\lambda_s < 0$), maximum $\Delta Z/Z$ of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}$ ($\lambda_s > 0$) is an order of magnitude lower (see Fig. 4).

Therefore, as-prepared Co-rich microwires with linear hysteresis loops are useful for applications involving GMI effect and magnetic softness. In contrast, in as-prepared Fe-rich microwires GMI effect is rather low and therefore they are suitable only for applications involving magnetic bistability or DW propagation. However, Co belongs to critical raw materials (Eggert, 2011). Therefore, potentially insecure supply and high price of Co could hinder the development of new applications. In this regard, less expensive Fe-rich amorphous glass-coated microwires are quite interesting for potential application considering a combination of high saturation magnetization, low cost and good mechanical and anti-corrosive properties. On the other hand, DW dynamics looks affected by the magnetostriction λ_s -value (higher DW velocities are observed for microwires with lower λ_s -values) (Zhukova *et al.*, 2020a). Therefore, even for applications involving DW dynamics, low magnetostrictive Co-rich microwires can be of interest.

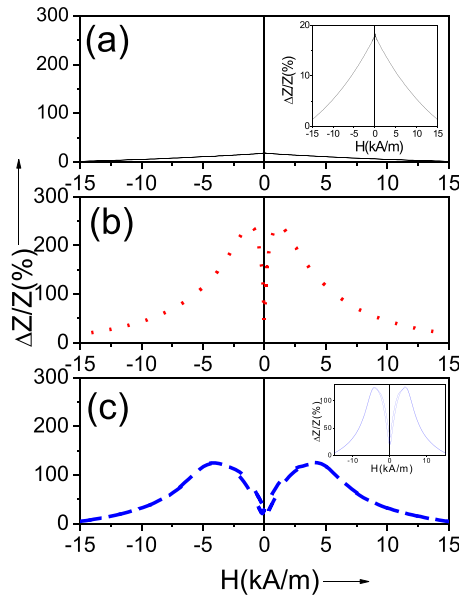


Fig. 4 $\Delta Z/Z(H)$ dependencies of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ (a) $\text{Co}_{67.1}\text{Fe}_{3.8}\text{Ni}_{1.4}\text{Si}_{14.5}\text{B}_{11.5}\text{Mo}_{1.7}$ (b), and $\text{Co}_{77.5}\text{Si}_{15}\text{B}_{7.5}$ (c) microwires measured at 500 MHz. Insets of a and c show a zoom of $\Delta Z/Z(H)$ dependencies. Adapted from Zhukov, A., Ipatov, M., Corte-León, P., *et al.*, 2020a. Giant magnetoimpedance in rapidly quenched materials. *J. Alloys Compd.* 814, 152225. Available at: <https://doi.org/10.1016/j.jallcom.2019.152225>.

As mentioned above, the theoretically predicted maximum GMI ratio is about 3000% (Kraus, 1999). Additionally, as evidenced from Figs. 2 and 3, the hysteresis loops are influenced by the magnetoelastic anisotropy. Therefore, it is expected that the development of advanced post-processing can help improve the GMI effect further, as well as the DW dynamics of the magnetic microwires.

Obviously, if the same microwire can present both properties, that is, the magnetic bistability with a corresponding fast DW propagation and the GMI effect, this can expand the application range.

Recently, several successful attempts on the optimization of magnetic softness of both Fe and Co-rich microwires as well as on the tuning of DW in both families of microwires have been reported (Zhukov *et al.*, 2013; Chiriac *et al.*, 2007; Corte-León *et al.*, 2021a,b; Zhukov *et al.*, 2017c; Zhukova *et al.*, 2019; Zhukov *et al.*, 2020c; Zhukov *et al.*, 2014a, 2014b; Gonzalez-Legarreta *et al.*, 2020a; Corte-León *et al.*, 2020c; Corte-León *et al.*, 2019a,b; Gonzalez-Legarreta *et al.*, 2020b; Zhukova *et al.*, 2018b; Zhukov *et al.*, 2021).

Below we will provide an overview of the routes allowing the optimization of magnetic properties paying attention on the post-processing of magnetic microwires.

Optimization of Magnetic Softness and GMI Effect in Magnetic Microwires

As discussed elsewhere (Knobel *et al.*, 2003; Zhukov *et al.*, 2015a; Phan and Peng, 2008; Dolabdjian and Ménard, 2017), the magneto-impedance effect can be observed in any ferromagnetic metals. However, as evidenced from Eq. (1) and discussed elsewhere (Usov *et al.*, 1998; Buznikov and Popov, 2021), the GMI effect value is linked to magnetic softness of ferromagnetic materials. One of the main parameters that affects the magnitude and the magnetic field dependence of the GMI effect (including off-diagonal components) of amorphous materials is the magnetic anisotropy and its spatial distribution (Panina and Mohri, 1994; Beach and Berkowitz, 1994; Knobel *et al.*, 2003; Zhukov *et al.*, 2015a; Phan and Peng, 2008; Usov *et al.*, 1998; Buznikov and Popov, 2021).

The main source of magnetic anisotropy of the amorphous materials is the magnetoelastic anisotropy. Therefore, tuning the magnetoelastic anisotropy of magnetic microwires is considered to be the main route to improve the GMI effect. The most common route is the selection of chemical composition with vanishing λ_s . However, even in magnetic microwires with vanishing λ_s the maximum GMI ratio is typically about an order of magnitude below the theoretically predicted maximum GMI ratio (see Fig. 4).

Routes of magnetic softness and GMI effect optimization in Co-rich magnetic microwires

Relaxation of internal stresses by appropriate heat treatment was considered to further magnetic softening and GMI effect improvement in Co-rich microwires with vanishing λ_s (Zhukova *et al.*, 2019; Zhukov *et al.*, 2020c; Zhukov *et al.*, 2014a; Gonzalez-Legarreta *et al.*, 2020a). In spite that heat treatment is considered as the most common method allowing stress relaxation, a magnetic hardening is observed in several Co-rich microwires (Zhukov *et al.*, 2014a; Zhukova *et al.*, 2019; Zhukov *et al.*, 2020c; Zhukov *et al.*, 2014a; Gonzalez-Legarreta *et al.*, 2020a).

One of the examples is provided in Fig. 5, where the effect of conventional furnace annealing on hysteresis loops of Co-rich ($\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.4}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$) microwire is provided. The annealing temperature, T_{ann} , is chosen in order to avoid the crystallization, i.e., below 400°C. Microwire $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.4}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ demonstrates substantial magnetic hardening similar to

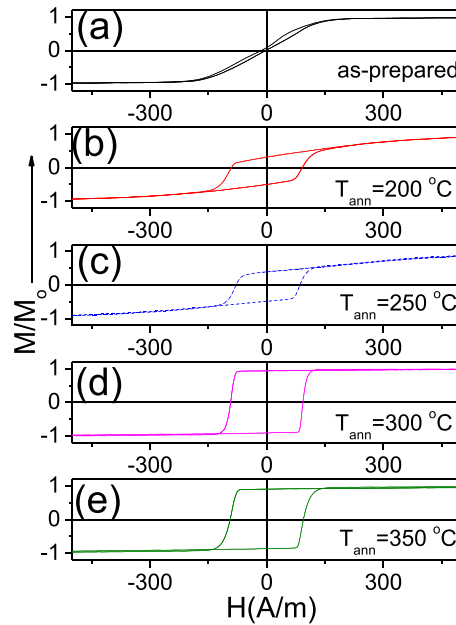


Fig. 5 Hysteresis loops of as-prepared (a) and annealed at 200°C (b), 250°C (c) 300°C (d) and 350°C (e) $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.5}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires. Reprinted with permission from Zhukova, V., Corte-Leon, P., Ipatov, M., *et al.*, 2019. Development of magnetic microwires for magnetic sensor applications. *Sensors* 19, 4767. Available at: <https://doi.org/10.3390/s19214767>.

other Co-rich microwires with vanishing λ_s – values (Zhukov *et al.*, 2014a, 2015b): the coercivity increases by more than an order of magnitude from 5 A/m to 90 A/m (see Fig. 5).

Such unexpected magnetic hardening has been explained considering the domain structure modification consisting of the growth of the inner axially magnetized domain at the expense of the outer domain shell as well as the change of the magnetostriction coefficient associated to the internal stresses relaxation (Zhukov *et al.*, 2014a, 2015b).

Obviously, conventional furnace annealing cannot be considered an optimal treatment for improving magnetic softness, at least for amorphous Co-rich microwires.

Although the deterioration of the GMI effect upon annealing, associated with magnetic hardening of Co-based microwires was previously reported (Zhukov *et al.*, 2015b); under same annealing conditions, an improvement in the GMI ratio can be observed. One such example is the GMI ratio improvement observed in $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.5}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires annealed at $T_{\text{ann}} = 300^\circ\text{C}$ and $T_{\text{ann}} = 350^\circ\text{C}$ (see Fig. 6(a,b) and Fig. 7(c)).

Such GMI ratio improvement looks rather surprising: the higher GMI ratio is observed for the annealed $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.5}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires, presenting almost perfect rectangular hysteresis loop (see Fig. 5(c,d,e)).

Stronger axial magnetic anisotropy of annealed $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.5}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire is also evidenced from $\Delta Z/Z(H)$ dependencies. Indeed, $\Delta Z/Z(H)$ dependence of $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.5}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire annealed at $T_{\text{ann}} = 300^\circ\text{C}$ measured up to $f = 100$ MHz present single-peak $\Delta Z/Z(H)$ dependence with a decay from $H = 0$ (see Fig. 6(a) and Fig. 7(a)) typical for axial magnetic anisotropy. However, the shape of $\Delta Z/Z(H)$ dependencies for as-prepared $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.5}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire measured at low f -values (10–100 MHz) has a double-maximum dependence typical for wires with circumferential magnetic anisotropy (see Figs. 6 (a,b) and 7(a)). Upon annealing, a decrease in the maximum magnetic field H_{max} is observed in the $\Delta Z/Z(H)$ dependences (see Fig. 6(a,b)). On the other hand, a transformation of single peak to double-peak $\Delta Z/Z(H)$ dependence of $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.5}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire annealed at $T_{\text{ann}} = 300^\circ\text{C}$ is observed at $f = 200$ MHz (see Fig. 6(b)). Additionally, an increase in H_{max} with increase in f is evidenced from Fig. 6(b). Such modification of $\Delta Z/Z(H)$ dependence with frequency as well as the double-peak $\Delta Z/Z(H)$ dependence of annealed $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.5}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire at elevated ($f \geq 200$ MHz) frequencies have been discussed in terms of circumferential magnetic anisotropy in the thin surface layer in annealed samples (Zhukov *et al.*, 2020c; Gonzalez-Legarreta *et al.*, 2020a). A transformation of $\Delta Z/Z(H)$ dependence from single-peak to double-peak type in this case should be observed when the thickness of such layer with circumferential magnetic anisotropy is comparable to the skin depth at a given frequency.

These experimental results are summarized in Fig. 7(c), where dependence of maximum GMI ratio, $\Delta Z/Z_{\text{max}}$ (defined as a maximum at a given frequency on $\Delta Z/Z(H)$ dependence for each sample) is provided. From these dependencies, it can be deduced that from the viewpoint of the GMI ratio optimization the conventional furnace annealing can be suitable under certain annealing conditions.

Although, under certain annealing conditions, an improvement in the GMI effect in $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.5}\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire is achieved, in most of publications on the effect of annealing on the GMI effect and the magnetic softness of various Co-rich microwires a deterioration of both the GMI effect and magnetic softness is reported (Zhukov *et al.*, 2014a, 2016).

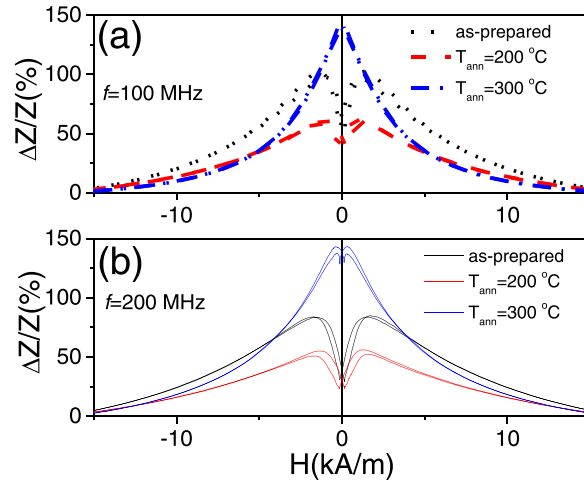


Fig. 6 $\Delta Z/Z(H)$ dependencies of as-prepared and annealed at different T_{ann} $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires measured at 100 (a) and 200 (b) MHz.

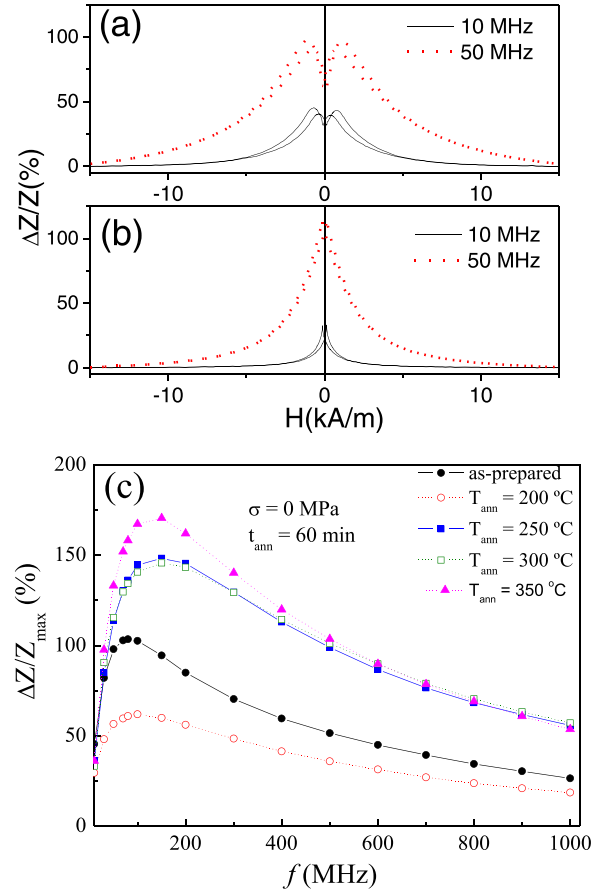


Fig. 7 $\Delta Z/Z(H)$ dependencies of as-prepared (a) and annealed at 300 °C (b) $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires and $\Delta Z/Z_{\text{max}}(f)$ dependencies for as-prepared and annealed $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires (c).

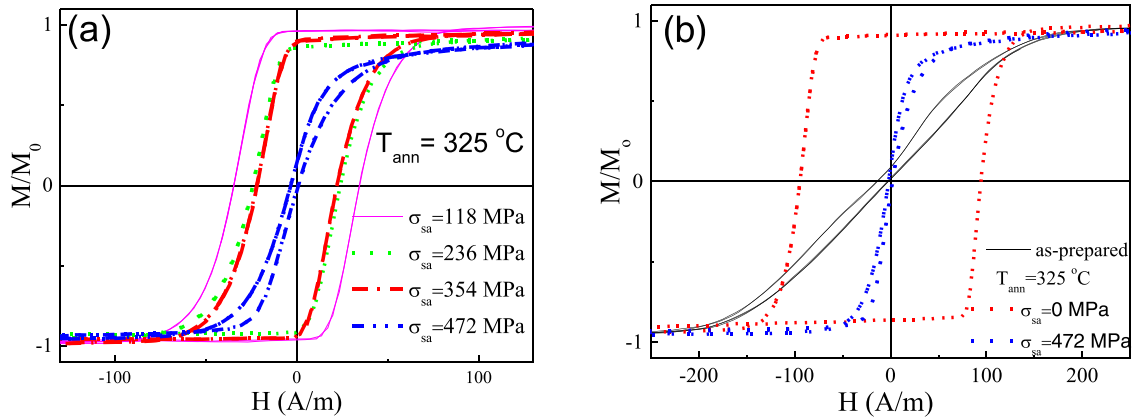


Fig. 8 Hysteresis loops of $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires stress-annealed at $T_{\text{ann}} = 325^\circ\text{C}$ and different σ_{sa} (a) and a comparison of hysteresis loops of as-prepared, annealed at $T_{\text{ann}} = 325^\circ\text{C}$ and stress-annealed at $T_{\text{ann}} = 325^\circ\text{C}$ and $\sigma_{\text{sa}} = 472$ MPa microwires (b). Reprinted with permission from Zhukov, A., Gonzalez-Legarreta, L., Corte-Leon, P., *et al.*, 2021. Tailoring of magnetic softness and magnetoimpedance of Co-rich microwires by stress-annealing. *Phys. Status Solidi A* 218. Available at: <https://doi.org/10.1002/pssa.202100130>.

In recent publications, it is reported that either stress-annealing or Joule heating is a more effective technique for optimization the magnetic properties of Co-rich microwires (Zhukov *et al.*, 2020a; Corte-León *et al.*, 2019a; Liu *et al.*, 2012; Corte-Leon *et al.*, 2020a; Zhukova *et al.*, 2019; Zhukov *et al.*, 2020c; Gonzalez-Legarreta *et al.*, 2020a,b; Zhukov *et al.*, 2021).

Several experimental results on the influence of stress-annealing on the magnetic properties of $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires are provided below. Stress-annealing is performed in conventional furnace in which the microwire was heated, annealed and slowly cooled with the furnace under tensile stress, σ_{sa} .

The influence of the annealing parameters (T_{ann} , t_{ann} , σ_{sa}) on the hysteresis loop of $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire subjected to stress-annealing is illustrated by Figs. 8 and 9.

A remarkable H_c increase is observed after conventional furnace annealing at $T_{\text{ann}} = 325^\circ\text{C}$ and $T_{\text{ann}} = 350^\circ\text{C}$ (see Figs. 8(b) and 9(b)). However, stress-annealing at the same T_{ann} allows a decrease in H_c . Such H_c decrease becomes more noticeable with an increase in σ_{sa} (see Figs. 8(a) and 9(a)).

Finally, under appropriate stress-annealing conditions (T_{ann} and σ_{sa}), better magnetic softness (lower H_c and H_k) is achieved in $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire. The most noticeable modifications of the hysteresis loops of $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire are a decrease in H_c and H_k after stress-annealing at high enough T_{ann} and σ_{sa} as compared to as-prepared $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire. In some sense, at high enough T_{ann} or σ_{sa} the hysteresis loop becomes linear (i.e., similar to those of as-prepared $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire), but with lower H_c and H_k (see Figs. 8(b) and 9(b)).

The observed modification of the hysteresis loops after annealing and stress-annealing has been discussed in terms of competition of internal stresses relaxation (attributed to annealing without stress) and transverse character of stress-annealing induced magnetic anisotropy (Gonzalez-Legarreta *et al.*, 2020b; Zhukov *et al.*, 2020a, 2021). In such case magnetic hardening observed upon annealing without stress can be explained by the growth of the inner axially magnetized core evidenced by the increase in remanent magnetization, M_r/M_0 , and almost independent on annealing temperature H_c -values (see Fig. 5). On the other hand, a transverse character of stress-annealing induced magnetic anisotropy is evidenced by Figs. 8 and 9. As observed, stress-annealing induced magnetic anisotropy depends on the stress-annealing conditions: T_{ann} , t_{ann} , σ_{sa} .

Naturally, a noticeable GMI ratio improvement is achieved in stress-annealed $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire exhibiting excellent magnetic softness (Gonzalez-Legarreta *et al.*, 2020b; Zhukov *et al.*, 2021).

Several examples are provided below. Gradual increase in $\Delta Z/Z_{\text{max}}$ increasing σ_{sa} at $T_{\text{ann}} = 300^\circ\text{C}$ and $T_{\text{ann}} = 350^\circ\text{C}$ can be appreciated from Fig. 10(a,b).

More than double $\Delta Z/Z_{\text{max}}$ ratio improvement is observed in $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire stress-annealed $T_{\text{ann}} = 300^\circ\text{C}$ and 350°C as compared to as-prepared microwire.

Stress-annealing also affects the shape of $\Delta Z/Z(H)$ dependencies. Generally, stress-annealed $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires present double-peak $\Delta Z/Z(H)$ dependence (see Figs. 10(a,b)). However, the magnetic field of the $\Delta Z/Z(H)$ maximum, H_m , becomes lower than that of the as-prepared sample. The difference in $\Delta Z/Z(H)$ dependence, $\Delta Z/Z_{\text{max}}$ and H_m -magnitudes for as-prepared and stress-annealed ($\sigma_{\text{sa}} = 472$ MPa) $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires is clearly observed in Fig. 11(a). As discussed elsewhere (Panina and Mohri, 1994; Beach and Berkowitz, 1994; Knobel *et al.*, 2003; Zhukov *et al.*, 2015a,b,c; Phan and Peng, 2008), H_m is linked to magnetic anisotropy field. Therefore, such evolution of $\Delta Z/Z(H)$ dependencies as well as lower H_m -magnitudes correlate quite well with observed modification of the hysteresis loops (see Figs. 8 and 9).

Furthermore, $\Delta Z/Z_{\text{max}}$ ratio improvement is achieved in the whole frequency range (see Fig. 11(b)): superior $\Delta Z/Z_{\text{max}}$ -magnitude is observed for all stress-annealed (at $\sigma_{\text{sa}} = 472$ MPa) $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires up to $f = 1$ GHz.

The optimum frequency for as-prepared $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire is about 80 MHz, while for stress-annealed $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires the optimal frequency shifts to about 150 MHz. The $\Delta Z/Z_{\text{max}}$ ratios of the

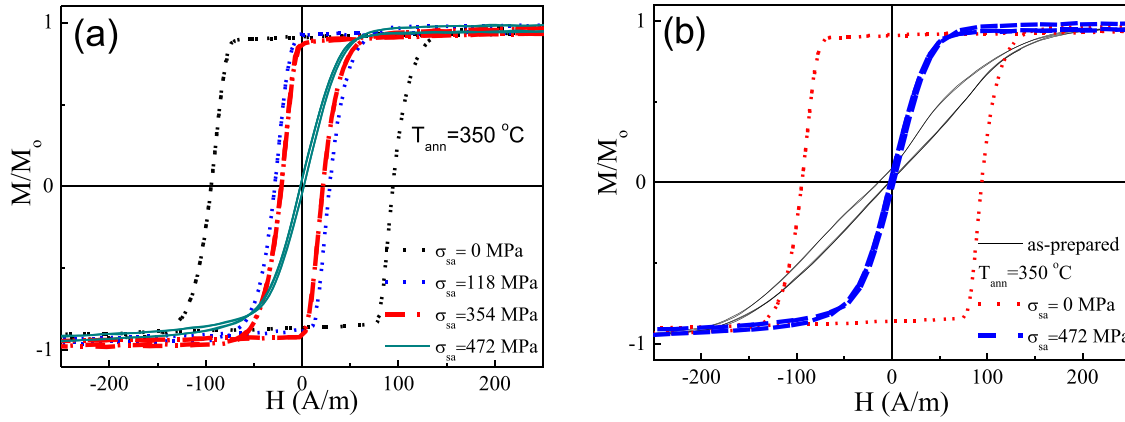


Fig. 9 Hysteresis loops of $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires annealed and stress-annealed at $T_{\text{ann}} = 350^\circ\text{C}$ at different σ_{sa} (a) and comparison of hysteresis loops of as-prepared, annealed at $T_{\text{ann}} = 350^\circ\text{C}$ and stress-annealed at $T_{\text{ann}} = 350^\circ\text{C}$ and $\sigma_{\text{sa}} = 472$ MPa microwires (b). Reprinted with permission from Zhukov, A., Gonzalez-Legarreta, L., Corte-Leon, P., *et al.*, 2021. Tailoring of magnetic softness and magnetoimpedance of Co-rich microwires by stress-annealing. Phys. Status Solidi A 218. Available at: <https://doi.org/10.1002/pssa.202100130>.

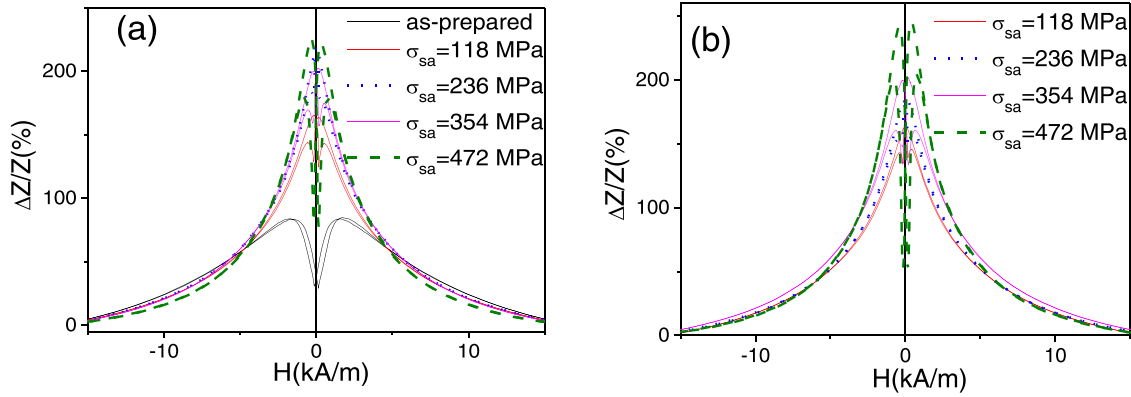


Fig. 10 $\Delta Z/Z(H)$ dependences of as-prepared and stress-annealed at $T_{\text{ann}} = 300^\circ\text{C}$ (a) and 350°C (b) $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire at different σ_{sa} measured at 200 MHz. Fig. 11(a). Reprinted with permission from Zhukova, V., Corte-Leon, P., Ipatov, M., *et al.*, 2019. Development of magnetic microwires for magnetic sensor applications. Sensors 19, 4767. Available at: <https://doi.org/10.3390/s19214767>.

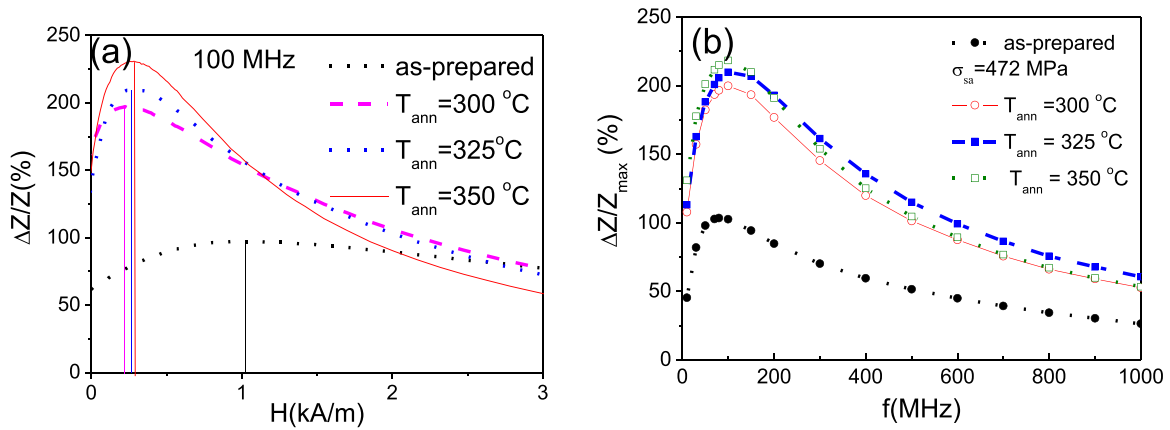


Fig. 11 $\Delta Z/Z(H)$ dependences of as-prepared and stress-annealed ($\sigma_{\text{sa}} = 472$ MPa) $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires measured at $f = 100$ MHz (a) and $\Delta Z/Z_{\text{max}}(f)$ dependences for the same samples (b). Reprinted with permission from Zhukov, A., Gonzalez-Legarreta, L., Corte-Leon, P., *et al.*, 2021. Tailoring of magnetic softness and magnetoimpedance of Co-rich microwires by stress-annealing. Phys. Status Solidi A 218. Available at: <https://doi.org/10.1002/pssa.202100130>.

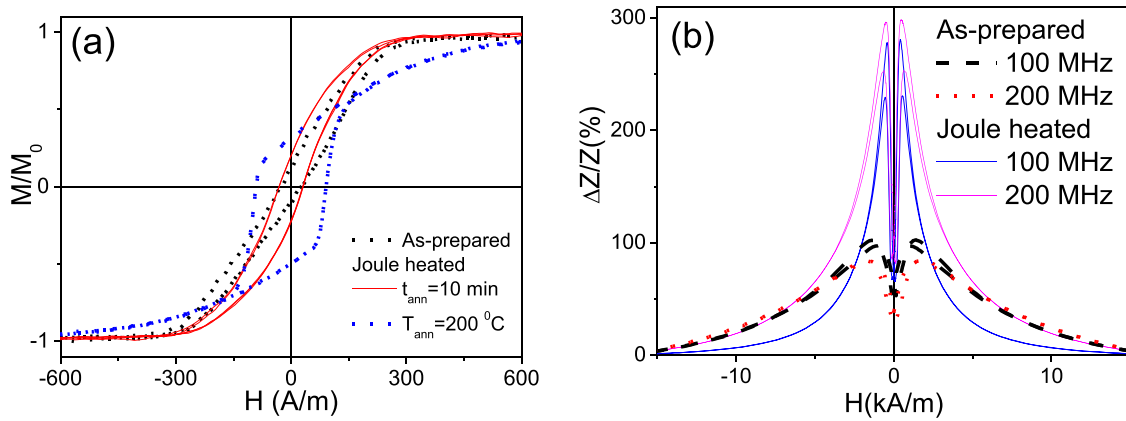


Fig. 12 Hysteresis loops of as-prepared and Joule heated (32 mA 10 min) and annealed at 200°C for 60 min samples (a), and $\Delta Z/Z(H)$ dependences of as-prepared and Joule heated $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{Si}_{1.1}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires (32 mA 10 min) (b).

stress-annealed samples are quite similar (of about 220%). For $f \leq 200$ MHz, the highest $\Delta Z/Z_{\max}$ ratio is observed for $T_{\text{ann}} = 350^\circ\text{C}$, while for $f \geq 200$ MHz slightly higher $\Delta Z/Z_{\max}$ ratio is observed for $T_{\text{ann}} = 325^\circ\text{C}$.

Similarly, GMI ratio improvement and a tendency in H_c decrease upon stress-annealing was reported in various Co-rich microwires with vanishing λ_s but different chemical composition (Zhukov *et al.*, 2017c; Zhukova *et al.*, 2017; Zhukova *et al.*, 2018c).

Consequently, we can resume that the stress-induced anisotropy allows tuning of both the GMI ratio value and the $\Delta Z/Z_{\max}(f)$ dependencies.

The origin of the induced magnetic anisotropy obtained by stress or magnetic field annealing in amorphous materials is discussed considering pair ordering mechanism as well as structural anisotropy originated either by residual bond anisotropy after removing the external stress, or by a residual strain (Luborsky and Walter, 1977; Haimovich *et al.*, 1985).

Accordingly, magnetic field annealing is potentially another possibility for tuning magnetic anisotropy of amorphous microwires.

Previously was shown that the annealing of Co-rich microwires under axial magnetic field enhances the axial magnetic anisotropy (Prieto *et al.*, 2000). Therefore, certain attention has been paid to Joule heating. The advantage of the Joule heating is that DC current flowing through the wire creates the circumferential magnetic field H_{circ} (also known as Oersted field) given as (Zhukova *et al.*, 2018a; Corte-León *et al.*, 2019a):

$$H_{\text{circ}} = I/2\pi r \quad (5)$$

where I is the current value, r - radial distance.

This H_{circ} varies from zero-value on the microwire axis to the maximum value exactly in the surface layer responsible for the GMI effect.

Perhaps such circumferential magnetic field allows avoiding the magnetic hardening of Co-rich microwires after Joule heating. One of the examples deals with the same $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{Si}_{1.1}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire, subjected to Joule heating for 10 min at 32 mA. Such Joule heating conditions have been selected to keep current density, j , low enough to avoid the excessive heating and the crystallization related to such heating.

From previous studies of the effect of Joule heating in amorphous materials (ribbons and conventional amorphous wires) is known, that Joule heating with $j \approx 30\text{--}45$ A/mm² produces the heating up to 400°C (Zhukova *et al.*, 2001; Blanco *et al.*, 1999). Theoretical estimations for glass-coated microwires ($d = 18$ μm) give similar temperatures for $I \approx 30$ mA (Astefanoaei *et al.*, 2006), although magnetic hardening and electrical resistivity change related to the crystallization process as well as estimations considering convection and radiation heat exchange together with magnetic and structural measurements indicate that the crystallization of a glass-coated microwires takes place at $j > 200$ A/mm² (Zhukova *et al.*, 2001; Popova *et al.*, 2018; Zhukov *et al.*, 2015c; Nematov *et al.*, 2020).

On the other hand, previously excellent magnetic softness and GMI ratio have been obtained in Co-rich microwire Joule heated at $j \approx 58$ and 78 A/mm² (Corte-León *et al.*, 2019a). For the $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{Si}_{1.1}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire with different d ($d = 22.8$ μm) $j \approx 78$ A/mm² corresponds to $I \approx 32$ mA.

The influence of Joule heating on the hysteresis loops and $\Delta Z/Z(H)$ dependences of $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{Si}_{1.1}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire are shown in Fig. 12. As observed, a slight decrease in H_c , evaluated from the hysteresis loops takes place, while the character of the hysteresis loops of Joule annealed $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{Si}_{1.1}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire generally remains similar to as-prepared sample (see Fig. 12(a)). As-compared to $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{Si}_{1.1}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire annealed at 200°C, for Joule heated $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{Si}_{1.1}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire lower H_c is observed (see Fig. 12(a)). Accordingly, Joule heating allows preventing magnetic hardening observed for conventional annealing and a substantial GMI ratio improvement, as observed from Fig. 12(b). An increase in $\Delta Z/Z_{\max}$ from $\Delta Z/Z_{\max} \approx 100\%$ to $\Delta Z/Z_{\max} \approx 300\%$ is evidenced from a comparison of $\Delta Z/Z(H)$ dependencies ($f = 100$ and 200 MHz) for as-prepared and Joule heated $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{Si}_{1.1}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires, respectively (see Fig. 12(b)). The Joule heated $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{Si}_{1.1}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire presents double-peak $\Delta Z/Z(H)$ dependencies, similar to those of as-prepared $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_{1.2}\text{Si}_{1.1}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire

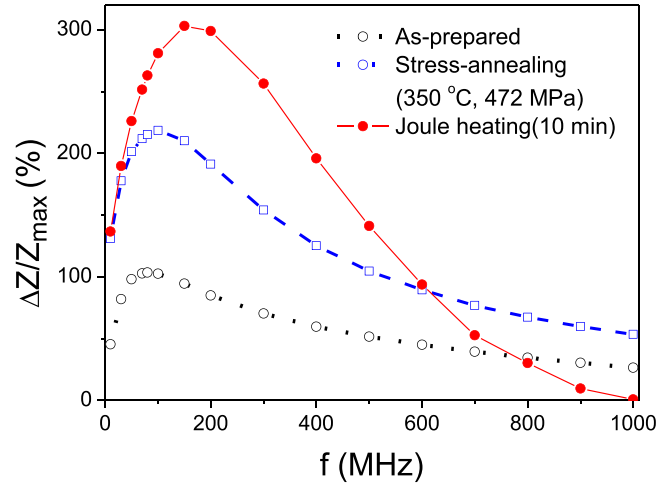


Fig. 13 $\Delta Z/Z_{max}(f)$ dependencies of Joule heated $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire. $\Delta Z/Z_{max}(f)$ dependencies of as-prepared and stress-annealed (at $T_{ann} = 350^\circ\text{C}$ for $\sigma_{sa} = 472$ MPa) are provided for comparison.

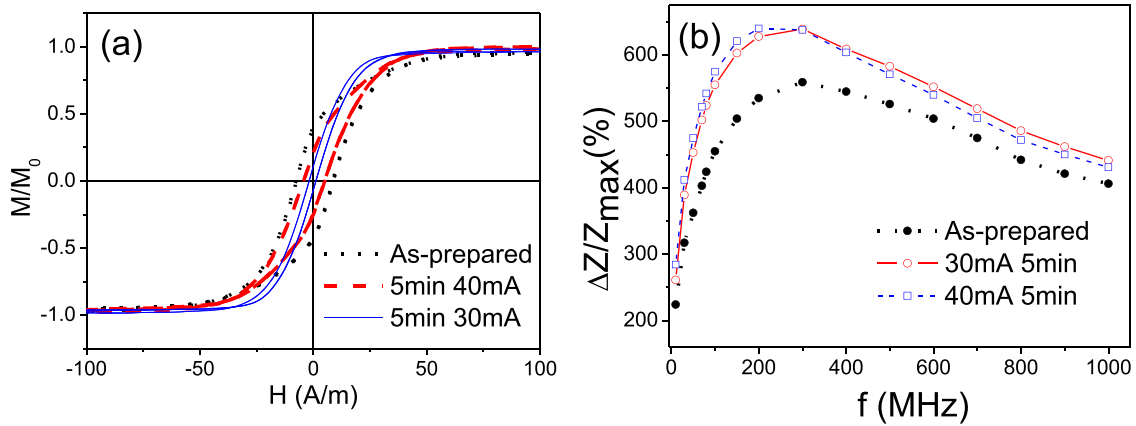


Fig. 14 Hysteresis loops (a) and $\Delta Z/Z_{max}(f)$ dependencies of as-prepared and Joule heated at 40 mA and 30 mA for 5 min (b) $\text{Co}_{67}\text{Fe}_{3.9}\text{Ni}_{1.5}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.6}$ amorphous glass-coated microwire. Adapted from Corte-León, P., Zhukova, V., Ipatov, M., *et al.*, 2019a. Engineering of magnetic properties of Co-rich microwires by joule heating. *Intermetallics* 105, 92–98.

(see Fig. 12(b)). Slightly lower H_m -value observed for Joule heated $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire (see Fig. 12(b)) correlates with lower H_k in Joule annealed $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire (Fig. 12(a)).

The most remarkable are better $\Delta Z/Z_{max}$ -values: $\Delta Z/Z_{max} \geq 300\%$ are evidenced at $f = 150\text{--}200$ MHz from Fig. 13.

Even higher, $\Delta Z/Z_{max}$ -values are obtained in $\text{Co}_{67}\text{Fe}_{3.9}\text{Ni}_{1.5}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.6}$. Similarly to the case of $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire, a decrease in the magnetic anisotropy field, H_k , up to about 30 A/m is observed upon Joule heating (see Fig. 14(a)). The difference between $\text{Co}_{67}\text{Fe}_{3.9}\text{Ni}_{1.5}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.6}$ and $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires is that the latter presents excellent soft magnetic properties already in as-prepared state: $H_k \approx 50$ A/m and $H_c \approx 8$ A/m (see Fig. 14(a)).

Additionally, Joule heated (30 mA, 5 min) $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire presents $H_c \approx 2$ A/m (Fig. 14(a)).

In contrast to $\text{Co}_{67}\text{Fe}_{3.9}\text{Ni}_{1.5}\text{B}_{11.5}\text{Si}_{14.5}\text{Mo}_{1.6}$ microwires, in the $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwires $\Delta Z/Z_{max} \approx 550\%$ is observed already in as-prepared state (Fig. 14(b)). These $\Delta Z/Z_{max}$ have been further improved by Joule heating, $\Delta Z/Z_{max} \approx 650\%$, $\text{Co}_{69.2}\text{Fe}_{3.6}\text{Ni}_1\text{B}_{12.5}\text{Si}_{11}\text{Mo}_{1.5}\text{C}_{1.2}$ microwire (see Fig. 14(b)).

Accordingly, stress-annealing and Joule heating of Co-rich microwires are prospective method allowing remarkable improvement of magnetic softness and GMI effect of Co-rich microwires.

Tuning of the magnetic softness and GMI effect in magnetic microwires

While properly processed Co-rich microwires can have excellent magnetic softness and remarkable GMI effect (see Figs. 9 and 14), Fe-based microwires are potentially very interesting materials, at least for the following reasons:

- (1) High price and insecure Co supplies, because Co belongs to critical raw materials.
- (2) Higher saturation magnetization of Fe-rich magnetic microwires.

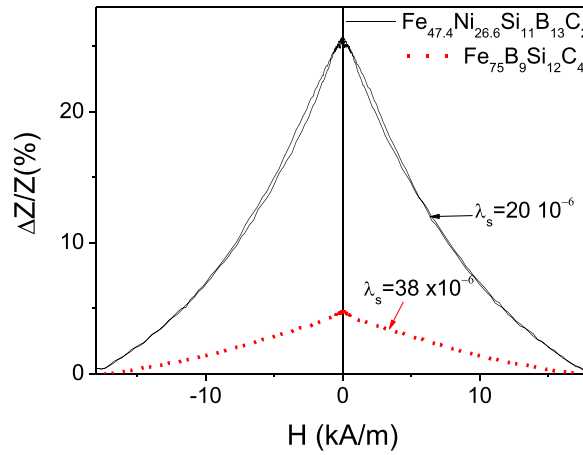


Fig. 15 $\Delta Z/Z(H)$ dependences of as-prepared $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ and $\text{Fe}_{47.4}\text{Ni}_{26.6}\text{Si}_{11}\text{B}_{13}\text{C}_2$ microwires measured at $f = 200$ MHz.

However, as-prepared Fe-rich microwires usually present rectangular hysteresis loops characterized by low initial magnetic permeability and relatively high (as-compared to Co-rich microwires) coercivity (see Fig. 1).

Therefore, studies aimed at finding effective post-processing methods that can improve the magnetic softness and the GMI effect in Fe-rich microwires have attracted a lot of attention in recent years (Corte-Leon *et al.*, 2021a,b,c; Corte-León *et al.*, 2019b).

As discussed above, the main factor limiting the magnetic softness of Fe-rich microwires is the high magnetoelastic anisotropy. In addition to $\text{Co}_x\text{Fe}_{1-x}$ amorphous alloys, the λ_s value can be reduced in $\text{Fe}_{1-x}\text{Ni}_x$ amorphous alloys by Ni doping. However, Ni-rich amorphous alloys present low saturation magnetization and Curie temperature. Therefore, the possibilities to reduce λ_s value by Ni doping are rather limited. Accordingly, the character of hysteresis loops of Fe-Ni rich microwires ferromagnetically ordered at room temperatures is similar to Fe-rich microwires (see Fig. 1). However, as seen from Fig. 15, slightly higher $\Delta Z/Z_{\max}$ can be obtained in Fe-Ni rich microwires with lower λ_s value. Such moderate $\Delta Z/Z_{\max}$ -values are commonly attributed to rectangular character of hysteresis loops related to strong axial magnetic anisotropy of microwires with positive λ_s -values. Such axially anisotropy is linked to the specific internal stresses distribution associated to the preparation method.

Consequently, most of recent publications deals with attempts to modify the magnetic anisotropy of glass-coated microwires with positive λ_s -values by appropriate post processing. One of such method is stress-annealing allowing to develop transverse magnetic anisotropy in amorphous materials.

Several experimental results on tuning of hysteresis loops and GMI effect in Fe-rich amorphous microwires are provided below.

We used Fe-rich microwire with typical composition ($\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$) and rather typical geometry ($d = 15,2 \mu\text{m}$; $D = 17,2 \mu\text{m}$) with high and positive magnetostriction coefficient ($\lambda_s \approx 38 \times 10^{-6}$) (see Table 2). Conventional annealing of such microwire ($T_{\text{ann}} = 300^\circ\text{C}$, $\sigma_{\text{sa}} = 0$) does not significantly affect the magnetic properties: the rectangular character of the hysteresis loop is retained and a slight decrease in H_c is observed persists (see Fig. 16(b)).

Stress-annealing substantially affects the hysteresis loops shape of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires: at the same T_{ann} a gradual change in the character of the hysteresis loop from rectangular to linear is observed with increasing σ_{sa} -values (see Fig. 16 (c-e)). Such modification in the hysteresis loops is reflected as a decrease in M_r/M_0 and H_c and increase in H_k (see Fig. 16(c-e)). Finally, rather strong transverse magnetic anisotropy is evidenced in $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires annealed at $T_{\text{ann}} = 300^\circ\text{C}$ and $\sigma_{\text{sa}} = 760$ MPa (see Fig. 16(e)).

A similar tendency is observed with an increase in T_{ann} at a fixed σ_{sa} : a gradual decrease in M_r/M_0 and H_c and an increase in H_k with an increase in T_{ann} are observed for $\sigma_{\text{sa}} = 190$ MPa (Fig. 17(b)). While, conventional annealing ($\sigma_{\text{sa}} = 0$ MPa) generally does not affect the overall shape of the hysteresis loops character: only slight H_c decreasing is observed (Fig. 17(a)).

The stress annealing time, t_{ann} , affects the hysteresis loops of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwire in a similar way, as T_{ann} . Only a slight decrease in H_c is observed in $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwire after annealing at $T_{\text{ann}} = 350^\circ\text{C}$ with t_{ann} increasing (see Fig. 18(a)). The hysteresis loops of the $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwire retain their rectangular shape (see Fig. 18(a)). However, the hysteresis loops shape of the stress-annealed samples change significantly: the rectangular hysteresis loop turns into an inclined one with increasing t_{ann} (see Fig. 18(b)).

Magnetic softening and effectivity of stress-annealing are evidenced from H_c evolution upon annealing and stress annealing summarized in Fig. 19. As can be appreciated, stress annealing produces a remarkable H_c decrease.

A similar influence of stress-annealing on the hysteresis loops of Fe-rich microwires is observed in Fe-rich microwires of various chemical compositions (Zhukov *et al.*, 2006; Zhukova *et al.*, 2003b). Consequently, the induction of transverse magnetic anisotropy under the stress annealing in Fe-rich microwires is of a general nature.

As shown below, transverse stress-annealing induced magnetic anisotropy allows not only magnetic softening bus also considerable GMI ratio improvement (Zhukov *et al.*, 2020a; Zhukova *et al.*, 2018a; Corte-Leon *et al.*, 2020c).

The most relevant difference of as- prepared and stress-annealed ($T_{\text{ann}} = 350^\circ\text{C}$, $t_{\text{ann}} = 60$ min and $\sigma_{\text{sa}} = 190$ MPa) $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires is the $\Delta Z/Z_{\max}$ -value: an order of magnitude $\Delta Z/Z_{\max}$ improvement GMI ratio is observed (see Fig. 20 (a,b)). Such difference is even more substantial at low frequency range (10–200 MHz). Additionally, stress-annealed $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$

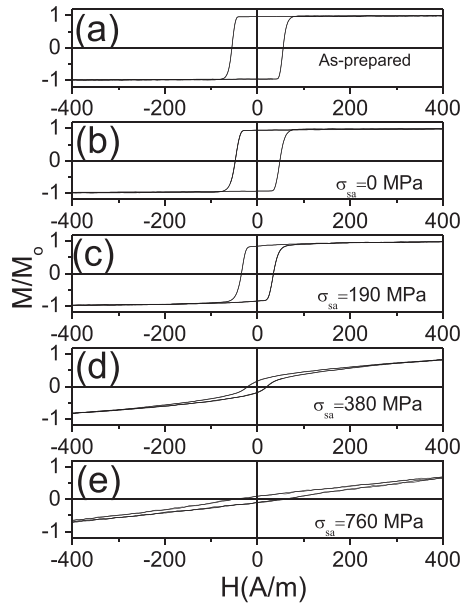


Fig. 16 Effect of tensile stress applied during the annealing at 300 °C ($t_{ann} = 60$ min) on hysteresis loops of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwire. (a-e) Reprinted with permission from Corte-Leon, P., Zhukova, V., Blanco, J.M., *et al.*, 2020c. Stress-induced magnetic anisotropy enabling engineering of magnetic softness of Fe-rich amorphous microwires. J. Magn. Magn. Mater. 510, 166939. Available at: <https://doi.org/10.1016/j.jmmm.2020.166939>.

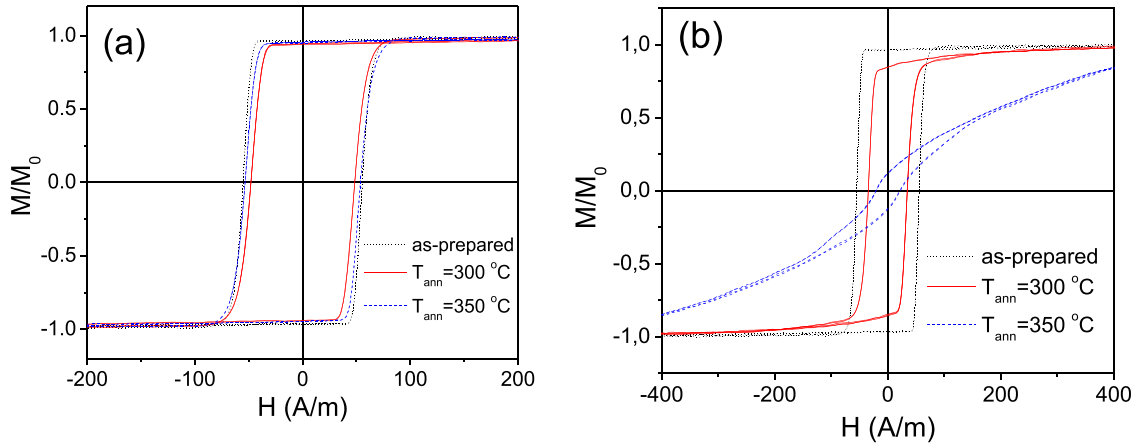


Fig. 17 Hysteresis loops of as-prepared and annealed for $t_{ann} = 60$ min at different T_{ann} of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires (a) and annealed at $\sigma_m = 190$ MPa for the same t_{ann} and T_{ann} of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires (b). Reprinted with permission from Corte-Leon, P., Zhukova, V., Blanco, J.M., *et al.*, 2020c. Stress-induced magnetic anisotropy enabling engineering of magnetic softness of Fe-rich amorphous microwires. J. Magn. Magn. Mater. 510, 166939. Available at: <https://doi.org/10.1016/j.jmmm.2020.166939>.

microwires present peculiar $\Delta Z/Z(H)$ dependencies: at low frequency (10–50 MHz) a single peak $\Delta Z/Z(H)$ dependence with a decay from $H = 0$ is observed (see Fig. 20(b)). Such $\Delta Z/Z(H)$ dependence is similar to that of as-prepared microwire and is typical for axial magnetic anisotropy (Usov *et al.*, 1998). However, at intermediate frequencies (100–400 MHz) $\Delta Z/Z(H)$ dependencies present irregular shape explained as the superposition of the double-peak $\Delta Z/Z(H)$ dependence typical for transverse magnetic anisotropy and the single-peak $\Delta Z/Z(H)$ dependence attributed to axial magnetic anisotropy (Zhukov *et al.*, 2021, 2019). At elevated frequencies ($f \geq 400$ MHz) $\Delta Z/Z(H)$ dependencies present double peak $\Delta Z/Z(H)$ dependence typical for the wires with transverse magnetic anisotropy (see Fig. 20(b)).

Such evolution of $\Delta Z/Z(H)$ dependencies with frequency has been interpreted considering the existence of the inner axially magnetized domain inside the stress-annealed microwires and the frequency dependence of the skin penetration depth, δ , as described in (Corte-Leon *et al.*, 2020c; Zhukov *et al.*, 2019).

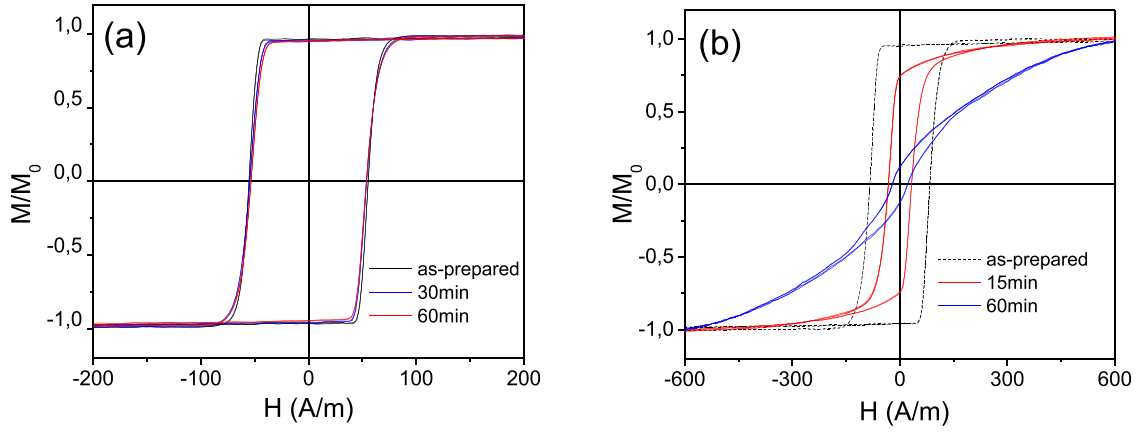


Fig. 18 Hysteresis loops of as-prepared and annealed (a) and stress-annealed for $\sigma_{sa} = 190$ MPa of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires (b) at $T_{ann} = 350^\circ\text{C}$ with t_{ann} as a parameter. Reprinted with permission from Corte-Leon, P., Zhukova, V., Blanco, J.M., *et al.*, 2020c. Stress-induced magnetic anisotropy enabling engineering of magnetic softness of Fe-rich amorphous microwires. J. Magn. Magn. Mater. 510, 166939. Available at: <https://doi.org/10.1016/j.jmmm.2020.166939>.

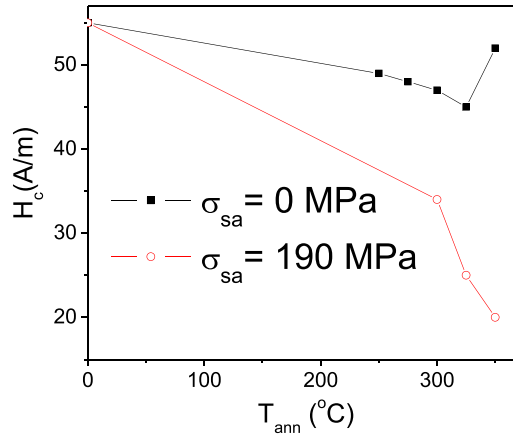


Fig. 19 Effect of annealing (0 MPa) and stress-annealing at $\sigma_{sa} = 190$ MPa on coercivity of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwire. Adapted from Corte-Leon, P., Zhukova, V., Blanco, J.M., *et al.*, 2020c. Stress-induced magnetic anisotropy enabling engineering of magnetic softness of Fe-rich amorphous microwires. J. Magn. Magn. Mater. 510, 166939. Available at: <https://doi.org/10.1016/j.jmmm.2020.166939>.

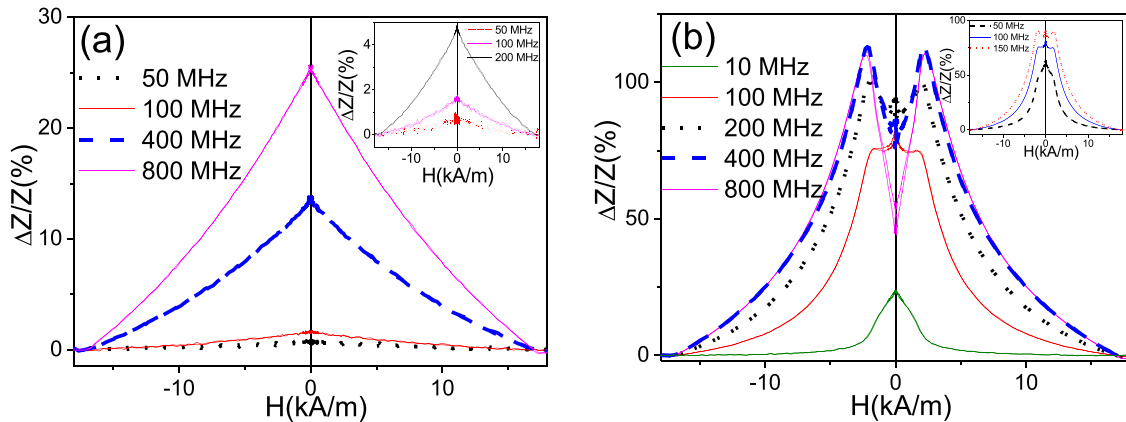


Fig. 20 $\Delta Z/Z(H)$ dependencies observed in as-prepared (a) and stress-annealed at $T_{ann} = 350^\circ\text{C}$ (for 60 min and $\sigma_{sa} = 190$ MPa) (b) $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires measured at different frequencies. Adapted from Corte-Leon, P., Zhukova, V., Blanco, J.M., *et al.*, 2020c. Stress-induced magnetic anisotropy enabling engineering of magnetic softness of Fe-rich amorphous microwires. J. Magn. Magn. Mater. 510, 166939. Available at: <https://doi.org/10.1016/j.jmmm.2020.166939>.

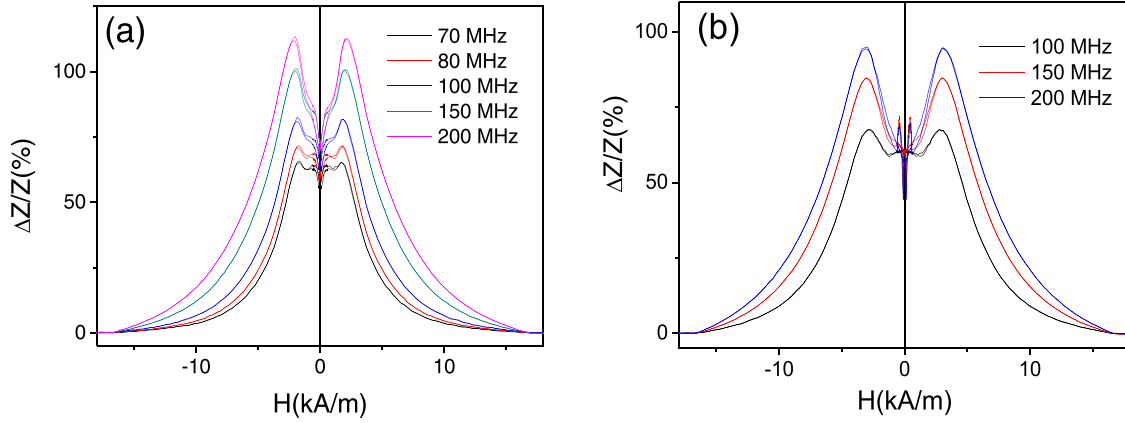


Fig. 21 $\Delta Z/Z(H)$ dependencies observed in stress-annealed at $T_{ann} = 250^\circ\text{C}$ for 60 min and $\sigma_m = 900$ MPa (a) and $T_{ann} = 300^\circ\text{C}$ for 60 min and $\sigma_m = 900$ MPa (b) $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires. Reprinted with permission from Corte-Leon, P., Zhukova, V., Blanco, J.M., *et al.*, 2020c. Stress-induced magnetic anisotropy enabling engineering of magnetic softness of Fe-rich amorphous microwires. *J. Magn. Magn. Mater.* 510, 166939. Available at: <https://doi.org/10.1016/j.jmmm.2020.166939>.

Similarly, irregular $\Delta Z/Z(H)$ dependencies are in fact observed in $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires stress-annealed at different conditions: mixed $\Delta Z/Z(H)$ dependencies of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires stress-annealed at $T_{ann} = 250^\circ\text{C}$ and 300°C ($t_{ann} = 60$ min and $\sigma_{sa} = 900$ MPa) (see Fig. 21(a,b)).

$\Delta Z/Z_{max}$ improvement by stress-annealing of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwire is evident from Fig. 22, where $\Delta Z/Z_{max}(f)$ dependencies are provided. The most remarkable $\Delta Z/Z_{max}$ improvement by stress-annealing is observed for the $f \leq 200$ MHz. Moreover, $\Delta Z/Z_{max}$ up to 120% is observed over a wide frequency range from 500 MHz to 1 GHz in the stress annealed $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwire (see Fig. 22).

The observed stress-annealing induced anisotropy presents partially reversible character: from recent studies of reversibility, it was found that part of such transverse stress-induced anisotropy can be annealed out (Corte-Leon *et al.*, 2021b; Zhukova *et al.*, 2018d).

As shown in Fig. 23(a-d), annealing at $T_{ann} = 350^\circ\text{C}$ (60 min) allows partial recovering of the stress-annealing induced anisotropy ($T_{ann} = 350^\circ\text{C}$, $t_{ann} = 60$ min, $\sigma_{sa} = 190$ MPa) evidenced by the change of the hysteresis loops character. The degree of reversibility depends on the subsequent annealing time. Longer annealing ($t_{ann} = 150$ min) allows one to recover M_r/M_0 up to almost the same values as for the as-prepared $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwire (see Fig. 23(d)). Lower coercivity, H_c , of the $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwire annealed for $t_{ann} = 150$ min (see Fig. 23(d)) can be attributed to the stress relaxation.

The reversibility degree is also affected by the stress-annealing conditions, such as σ_{sa} -value. Thus, stronger transverse stress-annealing magnetic anisotropy has been induced in the $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwire stress-annealed at $\sigma_{sa} = 760$ MPa (Fig. 24(b)). As observed from Fig. 24(c,d), such stress-annealing induced anisotropy ($T_{ann} = 350^\circ\text{C}$, $t_{ann} = 60$ min, $\sigma_{sa} = 760$ MPa) is almost irreversible, i.e., the hysteresis loops remains almost the same after subsequent annealing ($T_{ann} = 350^\circ\text{C}$, $t_{ann} = 60$ min and $T_{ann} = 350^\circ\text{C}$, $t_{ann} = 150$ min).

As mentioned above, the hysteresis loop shape and the remanent magnetization, M_r/M_0 , can provide useful information on the radial distribution of the magnetic anisotropy considering the core-shell domain structure model of magnetic wires (Mohri *et al.*, 1990; Vazquez and Chen, 1995). Thus, considering that the domain structure of magnetic wires consists of the inner axially magnetized core and an outer domain shell with radial magnetization orientation, the radius of the inner axially magnetized core, R_c , can be evaluated from M_r/M_0 as (Mohri *et al.*, 1990; Vazquez and Chen, 1995; Zhukova *et al.*, 2020a):

$$R_c = R(M_r/M_0)^{1/2} \quad (6)$$

where R is the microwire radius.

Although such model is initially proposed for magnetically bistable wires (Vazquez and Chen, 1995; Mohri *et al.*, 1990), it was used for evaluation of the magnetic anisotropy radial distribution of magnetic microwires subjected to stress-annealing (Corte-Leon *et al.*, 2020c; Corte-León *et al.*, 2019b).

Obtained $R_c(t_{ann})$ dependencies, evaluated from the hysteresis loops, show that most part of the metallic nucleus in stress-annealed at $\sigma_{sa} = 760$ MPa as well as in stress-annealed at $\sigma_{sa} = 760$ MPa subsequently annealed $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires present transverse magnetic anisotropy (see Fig. 24(e)). Only slight increase of M_r/M_0 and therefore, of R_c takes place in annealed out $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires (see Fig. 24(e) inset). Such slight $R_c(t_{ann})$ can be attributed to almost irreversible character of stress-annealing induced anisotropy at $\sigma_{sa} = 760$ MPa. In contrast, in stress-annealed at $T_{ann} = 350^\circ\text{C}$ for $\sigma_{sa} = 190$ MPa, most portion of stress-annealing induced anisotropy is reversible and can be annealed out (see Fig. 24(e)). Accordingly, from Fig. 23, 24, we can deduce that with an increase in σ_{sa} , the degree of irreversible stress-annealed magnetic anisotropy increases.

The remarkable feature of $\Delta Z/Z(H)$ dependencies of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires subjected to stress-annealing and subsequent annealing is that the irregular character of $\Delta Z/Z(H)$ dependencies typical for stress-annealed ($T_{ann} = 350^\circ\text{C}$) $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires is suppressed by subsequent annealing (see Fig. 25(a)). Additionally, $\Delta Z/Z_{max}$ -values of $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires subjected to stress-annealing and subsequent annealing is substantially higher in the wide frequency range (see Fig. 25(b)).

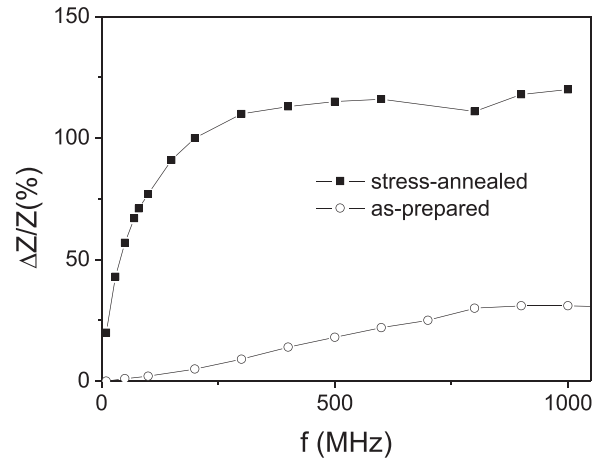


Fig. 22 Frequency dependence of $\Delta Z/Z_{\max}$ of as-prepared and stress-annealed ($T_{\text{ann}} = 350^\circ\text{C}$, $t_{\text{ann}} = 60$ min, $\sigma_{\text{sa}} = 190$ MPa) $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires. Reprinted with permission from Corte-Leon, P., Zhukova, V., Blanco, J.M., *et al.*, 2020c. Stress-induced magnetic anisotropy enabling engineering of magnetic softness of Fe-rich amorphous microwires. *J. Magn. Magn. Mater.* 510, 166939. Available at: <https://doi.org/10.1016/j.jmmm.2020.166939>.

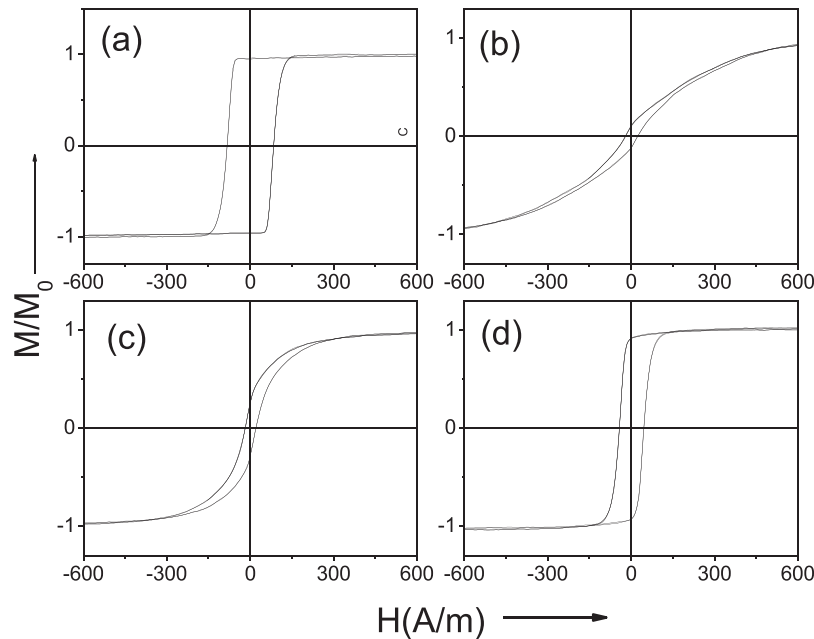


Fig. 23 Hysteresis loops of as-prepared (a), stress-annealed at $T_{\text{ann}} = 350^\circ\text{C}$, $t_{\text{ann}} = 60$ min, $\sigma_{\text{sa}} = 190$ MPa (b) and subsequently annealed for $t_{\text{ann}} = 60$ min (c) and for $t_{\text{ann}} = 150$ min (d) $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires. Reprinted with permission from Corte-Leon, P., Zhukova, V., Blanco, J.M., *et al.*, 2021b. Engineering of magnetic properties and magnetoimpedance effect in Fe-rich microwires by reversible and irreversible stress-annealing anisotropy. *J. Alloys Compd.* 855, 157460. Available at: <https://doi.org/10.1016/j.jallcom.2020.157460>.

Generally, magnetic field and stress-induced anisotropy in amorphous materials was discussed considering a few different mechanisms (1) the internal stresses redistribution during the stress-annealing due to “back stresses”, (2) the atomic directional pair ordering and (3) topological short range ordering or structural anisotropy (Luborsky and Walter, 1977; Haimovich *et al.*, 1985; Ohnuma *et al.*, 2012). The latter contribution is associated to the angular distribution of the atomic bonds and small anisotropic structural rearrangements at temperature near the glass transition temperature (Haimovich *et al.*, 1985; Ohnuma *et al.*, 2012).

Studied $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires contain only one ferromagnetic element (Fe). However, since T_{ann} is generally below Curie temperature (413°C) (Zhukova *et al.*, 2018b), this contribution cannot be completely excluded.

However, the partially reversible character of the stress-annealing induced magnetic anisotropy can be attributed to “back stresses” or to structural anisotropy mechanisms.

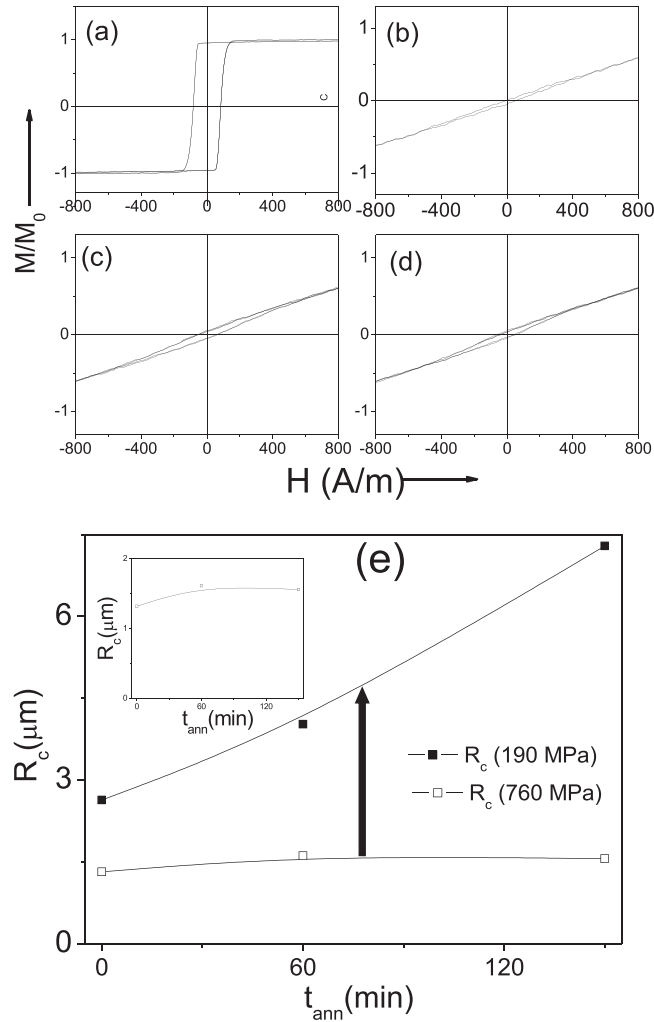


Fig. 24 Hysteresis loops of as-prepared (a), stress-annealed at $T_{ann} = 350^\circ\text{C}$ for $\sigma_{sa} = 760$ MPa (b) and subsequently annealed at $T_{ann} = 350^\circ\text{C}$ for 60 min (c) and $T_{ann} = 350^\circ\text{C}$ for 150 min (d) $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires. A comparison of $R_c(t_{ann})$ dependencies for the stress-annealed at $\sigma_{sa} = 760$ MPa and $\sigma_{sa} = 190$ and $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires (e). The lines in figure e are just guides for eyes. Reprinted with permission from Corte-Leon, P., Zhukova, V., Blanco, J.M., *et al.*, 2021b. Engineering of magnetic properties and magnetoimpedance effect in Fe-rich microwires by reversible and irreversible stress-annealing anisotropy. J. Alloys Compd. 855, 157460. Available at: <https://doi.org/10.1016/j.jallcom.2020.157460>.

The alternative route allowing magnetic softening of Fe-rich microwires is the devitrification by annealing of the amorphous precursor at sufficiently high temperature (Herzer, 1997; McHenry *et al.*, 1999). A few successful attempts to improve magnetic softness and GMI effect in Fe-rich microwires were reported (Zhukov *et al.*, 2017d, 2014b; Dudek *et al.*, 2007; Chiriac *et al.*, 1998; Talaat *et al.*, 2016). However, nanocrystalline microwires are rather brittle (Zhukova *et al.*, 2002a). Accordingly, the proposed route involving stress annealing of Fe-rich microwires presents several advantages: superior mechanical properties typical for amorphous materials and even better magnetic softness and higher GMI ratio as compared to nanocrystalline microwires.

Tuning of Magnetic Properties of Magnetic Microwires With Magnetic Bistability Effect

As already discussed above, amorphous magnetic microwires with positive magnetostriction coefficient, λ_s , usually present spontaneous magnetic bistability associated with a peculiar remagnetization process consisting of fast magnetization switching between two remanent states with opposite magnetization by a single and large Barkhausen jump (Zhukova *et al.*, 2020a). In contrast to conventional amorphous magnetic microwires prepared by in-rotating-water method, in which such magnetic bistability is observed in both positive and negative magnetostrictive compositions (Mohri *et al.*, 1990; Vazquez and Chen, 1995), in as-prepared glass-coated microwires spontaneous magnetic bistability is reported only for $\lambda_s > 0$ (Zhukova *et al.*, 2020a,b; Zhukov *et al.*, 2015c; Zhukova *et al.*, 2002b). Perfectly rectangular character of the hysteresis loops of magnetically bistable microwires is associated with the magnetization switching by ultrafast DW propagation along the microwire (Zhukova *et al.*, 2002b, 2014; Varga *et al.*, 2007).

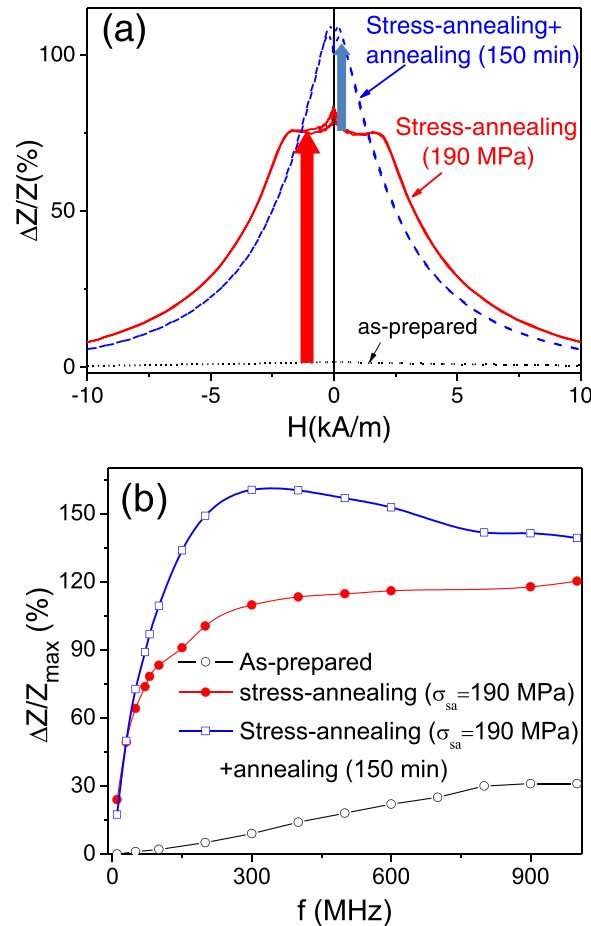


Fig. 25 $\Delta Z/Z(H)$ dependences of as-prepared, stress-annealed ($\sigma_{sa} = 190$ MPa) and stress-annealed ($\sigma_{sa} = 190$ MPa) + subsequently annealed ($t_{ann} = 150$ min) measured at 100 MHz (a) and $\Delta Z/Z_{\max}(f)$ dependence of the same samples and as-prepared sample (b). The lines in figure b are just guides for eyes. Adapted from Corte-Leon, P., Zhukova, V., Blanco, J.M., *et al.*, 2021b. Engineering of magnetic properties and magnetoimpedance effect in Fe-rich microwires by reversible and irreversible stress-annealing anisotropy. *J. Alloys Compd.* 855, 157460. Available at: <https://doi.org/10.1016/j.jallcom.2020.157460>.

Such magnetic materials with perfectly rectangular hysteresis loops are quite suitable for various magnetic sensors applications, like civil engineering, electronic surveillance (EAS), torque sensors, noncontact mechanocardiograph, racetrack memories, magnetic logics, etc., (Zhukova *et al.*, 2020a; Parkin *et al.*, 2008; Allwood *et al.*, 2005; Sabol *et al.*, 2017; Herzer, 2003; Zhukova *et al.*, 2021). Additionally, amorphous glass-coated microwires can present superior mechanical and anti-corrosive properties (Goto *et al.*, 1977; Zhukova *et al.*, 2002a). The Taylor-Ulitovsky technique allows preparation of about 1 km of continuous microwire from 1 g of metallic ingot and up to 10 km long continuous microwires (Baranov *et al.*, 2017; Zhukova *et al.*, 2021). In fact, one more advantage of the Taylor-Ulitovsky technique is that the microwire diameter could be substantially reduced (Ovári *et al.*, 2012; Baranov *et al.*, 2017). Such diameter decrease is essentially relevant for applications of magnetically bistable wires: a perfectly rectangular hysteresis loop can be observed for wires having a minimum length. Thus, in Fe-rich amorphous wires prepared by in-rotating method with diameters of about 120 μm such minimum length, L_m , for observation of rectangular hysteresis loop is about 7 cm (Mohri *et al.*, 1990; Vazquez and Chen, 1995). In contrast, $L_m \approx 2$ mm is reported for glass-coated microwires with $d \approx 10\text{--}15$ μm (Zhukova *et al.*, 2002b). Therefore, glass-coated microwires have a clear advantage: the magnetic sensors size can be drastically reduced (Zhukova *et al.*, 2021). Moreover, a flexible, thin, biocompatible and insulating glass-coating allows extending glass-coated microwires applications towards biomedicine, non-destructive monitoring external stimuli (stresses, temperature) in smart composites or construction health monitoring (Kozejova *et al.*, 2019; Sabol *et al.*, 2017; Qin and Peng, 2013; Mitxelena-Iribarren *et al.*, 2020; Zhukova *et al.*, 2021).

For most of such applications (i.e., EAS) tunability of the switching field, H_s , of magnetically bistable microwires is essentially relevant. One of such EAS applications is a multi-bit magnetic tags consisting of magnetically bistable microwires with rather different switching fields (Makhnovskiy *et al.*, 2011; Zhukova *et al.*, 2021; Zhukov, 2002). As evidenced from Figs. 1 and 2, a variety of H_s -values can be achieved either by compositional H_s dependence or by the effect of internal stress or thermal treatments on H_s .

Indeed, as can be appreciated from Fig. 2, for the same microwire composition, H_s can be modified by almost an order of magnitude (from 85 to 630 A/m) by changing the p -ratio. However, the problem for some applications is that for microwires with different d -values the magnetic moments with different d are rather different.

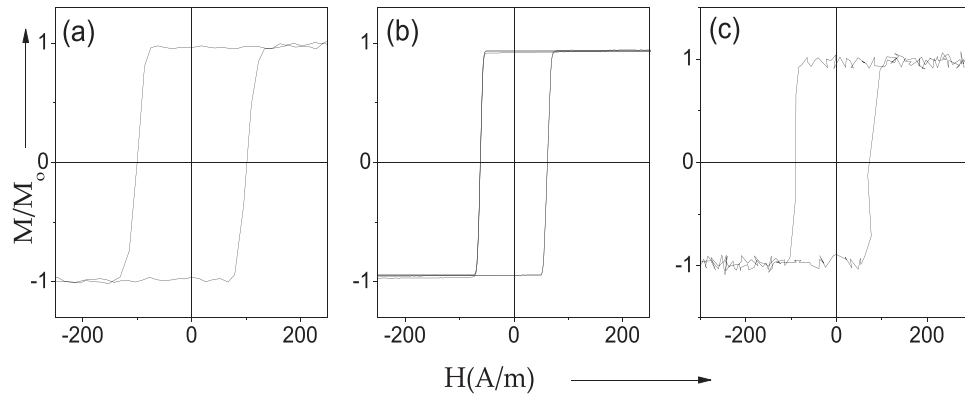


Fig. 26 Hysteresis loops of as-prepared $\text{Fe}_{77.5}\text{Si}_{7.5}\text{B}_{15}$ (a), $\text{Fe}_{47.4}\text{Ni}_{26.6}\text{Si}_{11}\text{B}_{13}\text{C}_2$ (b), and $\text{Fe}_{16}\text{Co}_{60}\text{Si}_{13}\text{B}_{11}$ (c) microwires. Reprinted with permission from ref. Zhukova, V., Corte-Leon, P., González-Legarreta, L., *et al.*, 2020a. Review of domain wall dynamics engineering in magnetic microwires. *Nanomaterials* 10 (12), 2407. Available at: <https://doi.org/10.3390/nano10122407>. Copyright © 2020 MDPI Publishing, Open Access.

The compositional dependence of H_s is evidenced from the hysteresis loops of $\text{Fe}_{77.5}\text{Si}_{7.5}\text{B}_{15}$ ($\lambda_s \approx 38 \times 10^{-6}$), $\text{Fe}_{47.4}\text{Ni}_{26.6}\text{Si}_{11}\text{B}_{13}\text{C}_2$ ($\lambda_s \approx 20 \times 10^{-6}$) and $\text{Fe}_{16}\text{Co}_{60}\text{Si}_{13}\text{B}_{11}$ ($\lambda_s \approx 15 \times 10^{-6}$) microwires (see Fig. 26).

The origin of the compositional H_s dependence of amorphous microwires is the compositional dependence of λ_s in $\text{Fe}_x\text{Co}_{1-x}$ and $\text{Fe}_x\text{Ni}_{1-x}$ amorphous alloys (Herzer, 1997; Churyukanova *et al.*, 2016).

An alternative approach is to use heat treatment, which allows relaxation of internal stresses while maintaining the magnetic moment values. For the $\text{Fe}_{75}\text{B}_9\text{Si}_{12}\text{C}_4$ microwires, annealing is not very effective: annealing allows only a slight H_s decrease (see Figs. 17(a) and 18 (a)). However, annealing is a more efficient way of H_s tuning in $\text{Fe}_{62}\text{Ni}_{15.5}\text{Si}_{7.5}\text{B}_{15}$ and $\text{Fe}_{49.6}\text{Ni}_{27.9}\text{Si}_{7.5}\text{B}_{15}$ microwires with positive magnetostriction ($\lambda_s \approx 27 \times 10^{-6}$ and 20×10^{-6} , respectively) (Zhukova *et al.*, 2020a; Zhukov *et al.*, 2015c; Zhukova *et al.*, 2020c).

Rectangular hysteresis loops are observed in as-prepared $\text{Fe}_{62}\text{Ni}_{15.5}\text{Si}_{7.5}\text{B}_{15}$ and $\text{Fe}_{49.6}\text{Ni}_{27.9}\text{Si}_{7.5}\text{B}_{15}$ microwires with positive λ_s values (approximately 27×10^{-6} and 20×10^{-6} , respectively) (see Fig. 27(a) and Fig. 28(a)). Such rectangular character of the hysteresis loop is maintained for all annealed $\text{Fe}_{62}\text{Ni}_{15.5}\text{Si}_{7.5}\text{B}_{15}$ and $\text{Fe}_{49.6}\text{Ni}_{27.9}\text{Si}_{7.5}\text{B}_{15}$ microwires (at $T_{\text{ann}} = 410^\circ\text{C}$) (see Figs. 27 and 28). However, a remarkable increase in H_s is observed in both Fe-Ni based microwires upon annealing (see Figs. 27 and 28).

The very beginning of crystallization in Fe-Ni-based microwires is observed only upon at $T_{\text{ann}} = 435^\circ\text{C}$ (Zhukov *et al.*, 2015c). Therefore, the observed magnetic hardening upon annealing of $\text{Fe}_{62}\text{Ni}_{15.5}\text{Si}_{7.5}\text{B}_{15}$ and $\text{Fe}_{49.6}\text{Ni}_{27.9}\text{Si}_{7.5}\text{B}_{15}$ microwires has been attributed to the DW stabilization effect (Zhukova *et al.*, 2020b,c).

The mechanism responsible for DW stabilization is linked with the directional atomic pair ordering along the preferred magnetization direction during annealing and is usually observed in amorphous alloys with two or more ferromagnetic elements (Ohnuma *et al.*, 2012). The non-monotonic $H_c(t_{\text{ann}})$ dependence (see Fig. 28(e)) was explained in terms of the simultaneous effect of internal stresses relaxation (allowing a decrease in H_c) and DW stabilization (leading to an increase in H_c) (Zhukova *et al.*, 2021, 2020c).

Observed possibility to tune coercivity of Fe-Ni based microwires by annealing, make them suitable for several applications including multi-bit tags security applications (Zhukova *et al.*, 2021, 2020c).

An even wider H_s range can be obtained by partial or complete devitrification of amorphous microwires. Although generally magnetic softening is observed upon devitrification of amorphous precursor (Herzer, 1997), in several glass-coated microwires the rectangular character of the hysteresis loops is maintained even in nanocrystalline state (Zhukova *et al.*, 2020b; Zhukov *et al.*, 2017d; Zhukova *et al.*, 1999).

As shown in Fig. 29 (a-c), as-prepared Finemet-like ($\text{Fe}_{70.8}\text{Cu}_1\text{Nb}_{3.1}\text{Si}_{14.5}\text{B}_{10.6}$), Hitperm-like ($\text{Fe}_{38.5}\text{Co}_{38.5}\text{B}_{18}\text{Mo}_4\text{Cu}_1$) and the ($\text{Fe}_{0.7}\text{Co}_{0.3}$)_{83.7} $\text{Si}_4\text{B}_8\text{P}_{3.6}\text{Cu}_{0.7}$ glass-coated microwires present perfectly rectangular hysteresis loops with elevated (up to 500 A/m) H_s -values. On the other hand, rectangular hysteresis loop can be observed in nanocrystalline microwires devitrified by annealing of an amorphous precursor (Zhukova *et al.*, 2020b, 1999, 2015, 2021). Thus, rectangular hysteresis loop with $H_c \approx 2000$ A/m is observed in $\text{Fe}_{71.8}\text{Cu}_1\text{Nb}_{3.1}\text{Si}_{15}\text{B}_{9.1}$ microwire ($\rho = 0.282$) annealed at $T_{\text{ann}} = 700^\circ\text{C}$ (see Fig. 29(d)).

The main advantage of nanocrystalline alloys is high saturation magnetization (Herzer, 1997). Unfortunately, nanocrystalline materials obtained by annealing of amorphous precursor usually present poorer mechanical properties (Zhukova *et al.*, 2002a). The advantage of as-prepared nanocrystalline materials is that they can present better mechanical properties (Zhukova *et al.*, 2020b, 2020d, 2015).

A predictable design of rectangular hysteresis loops by selection of the chemical composition of the metallic nucleus, by controlling of the internal stresses value (through the glass-coating thickness), and by appropriate annealing can serve as a good basis for prospective applications of magnetically bistable microwires.

Future Directions

Although the described routes for optimizing the magnetic properties allowed for a significant improvement in magnetic softness and an increase in the GMI effect, the obtained GMI ratio values are still below the theoretically predicted values. Therefore, further

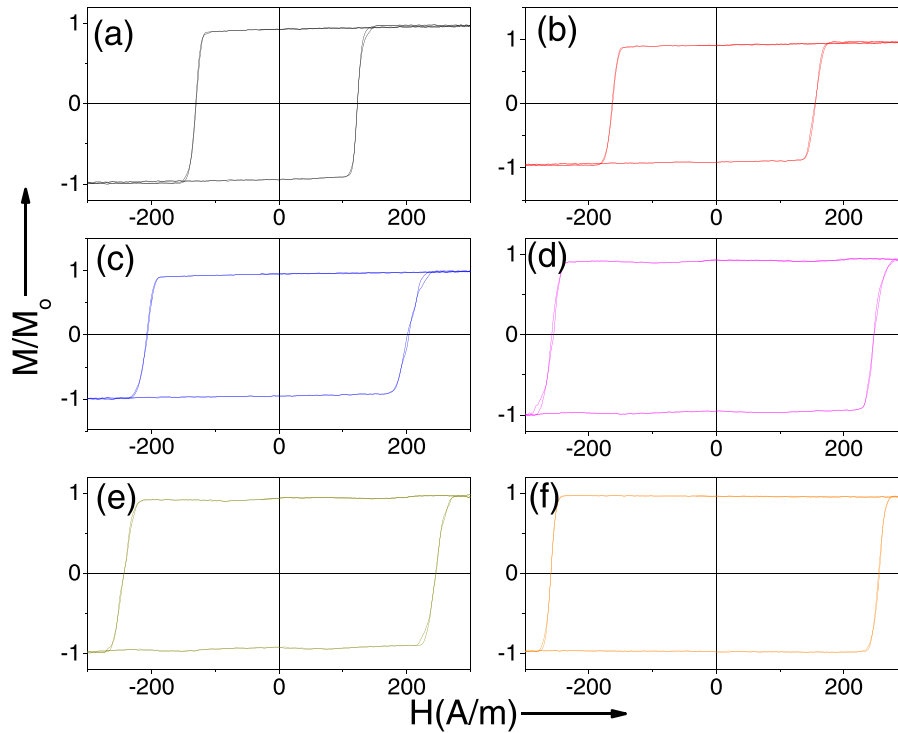


Fig. 27 Hysteresis loops of as-prepared (a) and annealed at $T_{ann} = 410^\circ\text{C}$ for 4 min (b), 16 min (c) 32 min (d), 64 min (e) and 256 min (f) $\text{Fe}_{62}\text{Ni}_{15.5}\text{Si}_{7.5}\text{B}_{15}$ microwires. Reproduced with permission from ref. Zhukova, V., Corte-Leon, P., González-Legarreta, L., *et al.*, 2020b. Optimization of magnetic properties of magnetic microwires by post-processing. Processes 8, 1006. Available at: <https://doi.org/10.3390/pr8081006>.

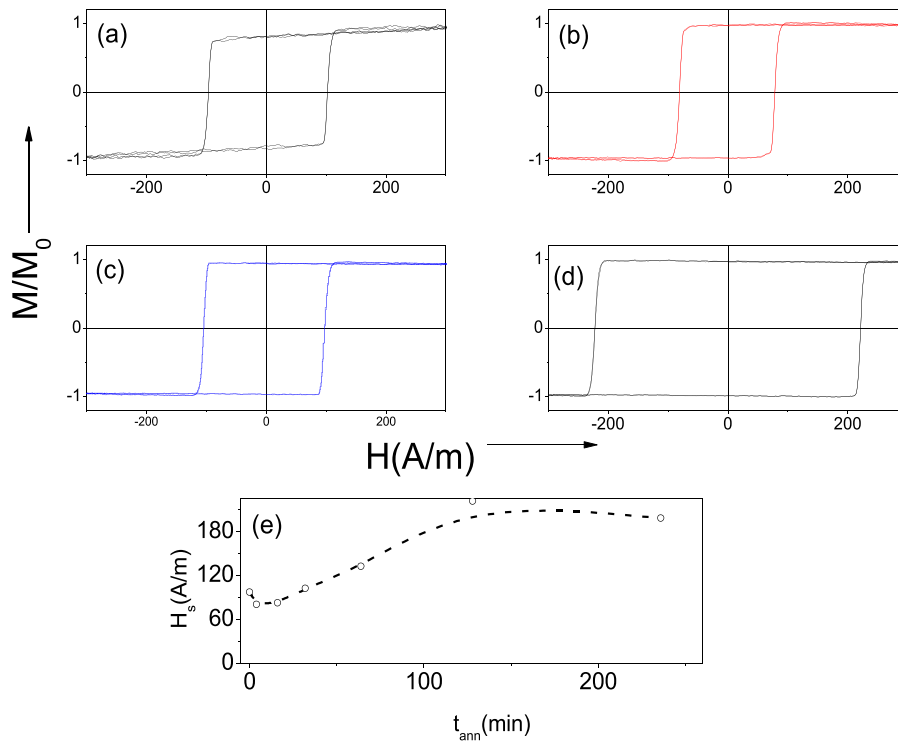


Fig. 28 Hysteresis loops of as-prepared (a) and annealed at $T_{ann} = 410^\circ\text{C}$ for $t_{ann} = 4$ min (b) 32 min (c) 128 min (d) and $H_c(t_{ann})$ dependence (e) for $\text{Fe}_{49.6}\text{Ni}_{27.9}\text{Si}_{7.5}\text{B}_{15}$ microwires. The line in Figure (e) is just a guide to the eyes. Reproduced with permission from Zhukova, V., Talaat, A., Corte-Leon, P., *et al.*, 2020c. Engineering of magnetic properties and domain wall dynamics in Fe-Ni-based amorphous microwires by annealing. AIP Adv. 10, 015130. Available at: <https://doi.org/10.1063/1.5130173>.

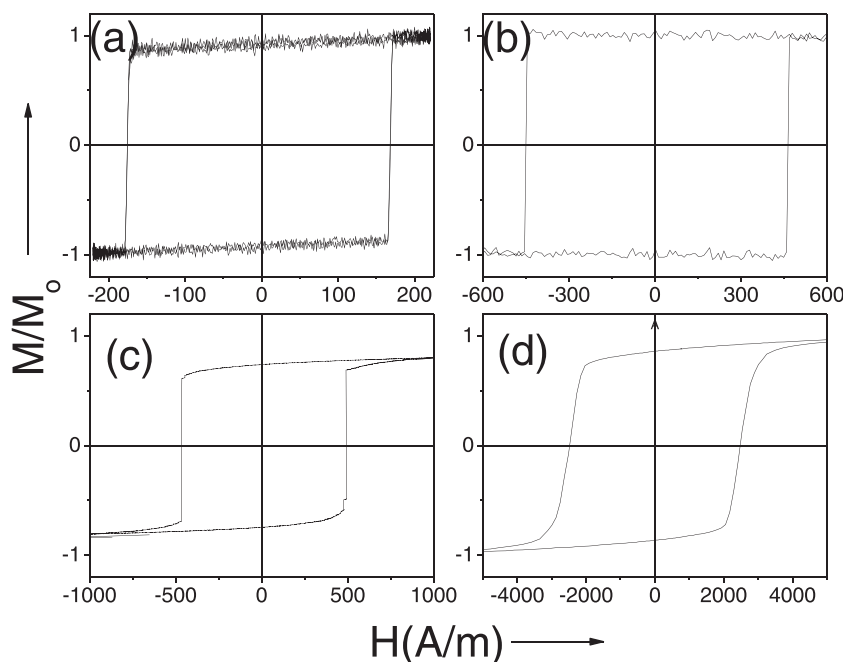


Fig. 29 Hysteresis loops of as-prepared $\text{Fe}_{70.8}\text{Cu}_1\text{Nb}_{3.1}\text{Si}_{14.5}\text{B}_{10.6}$ ($\rho = 0.38$) (a); $\text{Fe}_{38.5}\text{Co}_{38.5}\text{B}_{18}\text{Mo}_4\text{Cu}_1$ ($\rho = 0.6$) (b); $(\text{Fe}_{0.7}\text{Co}_{0.3})_{83.7}\text{Si}_4\text{B}_8\text{P}_{3.6}\text{Cu}_{0.7}$ ($\rho = 0.84$) (c) and annealed at $T_{\text{ann}} = 700^\circ\text{C}$ $\text{Fe}_{71.8}\text{Cu}_1\text{Nb}_{3.1}\text{Si}_{15}\text{B}_{9.1}$ ($\rho = 0.282$) (d) microwires. Adapted from Zhukova, V., Corte-Leon, P., González-Legarreta, L., *et al.*, 2020b. Optimization of magnetic properties of magnetic microwires by post-processing. Processes 8, 1006. Available at: <https://doi.org/10.3390/pr8081006>. Zhukova, V., Cobeño, A.F., Zhukov, A., *et al.*, 1999. Coercivity of glass-coated $\text{Fe}_{73.4-x}\text{Cu}_1\text{Nb}_{3.1}\text{Si}_{13.4} + x\text{B}_{9.1}$ ($0 \leq x \leq 1.6$) microwires. Nanostruct. Mater. 11, 1319–1327. Available at: [https://doi.org/10.1016/S0965-9773\(99\)00424-9](https://doi.org/10.1016/S0965-9773(99)00424-9). Zhukova, V., Ipatov, M., Corte-Leon, P., *et al.*, 2020d. Excellent magnetic properties of $(\text{Fe}_{0.7}\text{Co}_{0.3})_{83.7}\text{Si}_4\text{B}_8\text{P}_{3.6}\text{Cu}_{0.7}$ ribbons and microwires. Intermetallics 117, 106660. Available at: <https://doi.org/10.1016/j.intermet.2019.106660>.

efforts are needed to find suitable post-processing methods to improve the properties of the magnetic microwires (with higher GMI ratio, better magnetic softness, wider switching field range).

On the other hand, recently the unique combinations of magnetic properties, such as a high GMI effect and fast magnetization switching related to a single and large Barkhausen jump in the same magnetic microwires, subjected to specially developed post-processing are realized (Corte-Leon *et al.*, 2021a, 2020d). Such "universal" magnetic microwires may be of interest for new multifunctional device applications.

Finally, the unique combination of excellent magnetic properties with superior mechanical properties, high corrosion resistance, biocompatibility and reduced dimensionality is potentially suitable for completely new applications such as new wireless sensor technologies for structural stress and integrity monitoring in civil engineering, biomedical applications, process control, etc.

Therefore, new applications are expected to be developed using high-performance, durable, robust and cost-effective magnetic microwires.

Conclusions

In this article, we have evaluated several routes allowing the development of magnetic microwires coated by a flexible, insulating and biocompatible glass-layer, fulfilling the increasing demands of advanced sensing applications, such as low cost, good functional (magnetic, mechanical, corrosive) properties, and tunability of these properties.

The GMI effect can be obtained in as-prepared Co-rich microwires. However, the magnetic softness and GMI performance of these Co-rich amorphous microwires can be further improved by an appropriate thermal treatment (including stress-annealing and Joule heating). The MI ratio of as-prepared Fe-rich amorphous microwires with positive magnetostriction coefficient is generally rather low. Therefore, appropriate post-processing is essentially relevant for GMI applications of Fe-rich microwires. The magnetic softening and the GMI effect improvement (an order of magnitude) are achieved in Fe-rich microwires by stress-annealing and combined stress-annealing, followed by conventional furnace annealing. In magnetically bistable amorphous microwires with positive magnetostriction, the switching field values can be tuned by modification of the chemical composition, tuning of the internal stresses, or through an appropriate heat treatment (including devitrification of the amorphous precursor).

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Ferromagnetic Microwire Metacomposites

Diana Estevez and Faxiang Qin, Institute for Composites Science Innovation, School of Materials Science and Engineering, Zhejiang University, Hangzhou, PR China

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Abstract

Metamaterials are one of the most important scientific breakthroughs that have shaped the dynamic field of materials science. Nevertheless, their high manufacturing costs derived from their complicated structures hamper their mass production. Additionally, their ultimate properties are not dependent on the intrinsic properties of the constituents but rather on the internal and specific metamaterial structure, making them merely “meta-structures”. Therefore, the concept of metacomposite has been proposed to account for a real composite material with metamaterial characteristics having a much simplified structure and broader application prospects. Among them, an easily manufactured and versatile metacomposite enabled by ferromagnetic microwires has been established, which is the main focus of this chapter. We first demonstrate that a bias free-double negative (DNG) feature is obtained for the most basic configuration, i.e., Fe-based microwires arranged in a parallel manner. We then move to discuss the different optimization strategies of microwire metacomposites based on meso/microstructural parameters, in-built vertical interfaces, hybridization, and external stimuli. Remarkable features of the optimized composites such as improved DNG performance, directional DNG switching, stimuli-responsive transmission windows and Lorentz-to-Drude dispersion transition are also thoroughly discussed. Next, the up-to-date manufacturing process of microwire metacomposites and their unparalleled advantages in microwave sensing and cloaking areas are presented. Finally, the chapter is closed with an outlook on further strategies and perspectives for improving the discussed microwire metacomposites.

Key Points

- Ferromagnetic microwire metacomposites are introduced which account for real composites with metamaterial characteristics with a much simplified structure and fabrication process.
- Different optimization strategies based on meso/microstructural parameters, in-built vertical interfaces, hybridization, and external stimuli are discussed.
- Remarkable features of optimized metacomposites are thoroughly explored.
- Up-to-date manufacturing process of microwire metacomposites and their unparalleled advantages in microwave sensing and cloaking areas are presented.

Introduction

Since the early 2000s, metamaterials have emerged as a rapidly growing forefront subject in areas involving physics and materials science. They are mainly categorized as artificially engineered materials with unusual electromagnetic (EM) properties that are not found in naturally occurring materials. Historically, in 1968, Veselago foresaw the possibility of negative refractive index from acquiring simultaneously negative permittivity (ϵ) and permeability (μ), i.e., double-negative (DNG) characteristic (Veselago, 1968). However, it was not until the late 1990s that such concept emerged from obscurity when Sir Pendry realized experimentally negative permittivity through an array of parallel metallic wires (Pendry *et al.*, 1996). Actually, obtaining negative permittivity is hardly an issue considering that some “natural” materials such as ferroelectrics exhibit this characteristic. The real challenge was achieving artificial negative permeability from non-magnetic materials which led to the development of a periodic lattice structure consisting of split ring resonators (SRRs) (Pendry *et al.*, 1999). Remarkably, in 2001, Shelby *et al.* (2001) experimentally demonstrated a DNG feature in a structure comprising of parallel wires and SRRs which instantly attracted tremendous interest from both academia and industry. To date, a considerable amount of research programmes and grants have been dedicated to understand, design and develop metamaterials and their prospective applications. These efforts have borne fruit and the palette of metamaterials has extended from electromagnetics (Shalaev, 2007) to thermal (Li *et al.*, 2021) acoustic (Bacigalupo *et al.*, 2020) and mechanical metamaterials (Bückmann *et al.*, 2014). By definition, metamaterials are artificial structures comprised of periodically arranged building blocks. To understand metamaterials, the DNG property is the most important feature. In the realm of electromagnetics, the overall EM response can be averaged by considering the material as a homogeneous medium characterized by both ϵ and μ . Such consideration enables to control the propagation of EM waves based on tailoring the ϵ and μ through macro-/mesostructural parameters, such as dimensions and periodicity. The freedom of designing EM properties e.g., DNG or single negative (SNG) features has conveyed a number of applications in artificial magnetism (Pendry *et al.*, 1999; Smith *et al.*, 2000) high resolution medical imaging (Kim and Rho, 2015) EM cloaks (Yang *et al.*, 2012) and perfect metamaterial absorbers (Zamzam *et al.*, 2021).

Despite the flourishing of metamaterials, their peculiar physical properties derive purely from a periodical structure rather than from the intrinsic material's properties. This proves disadvantageous for multifunctional purposes owing to the lack of flexibility and tunability with external stimuli such as magnetic bias or stress. Complicated internal topologies are also necessary to achieve DNG

characteristics, which requires delicate processing techniques to enable precise dimension control comparable to/smaller than the EM wavelength. These shortcomings restrain metamaterials for mass production and hence engineering manufacturing technologies are urgently in demand. Since essentially metamaterials constitute a composite structure, multifunctionalities could be approached from composite perspective. Therefore, the term “metacomposite” is proposed, which has been used to define composite structures that possess metamaterials properties in e.g., acoustic (Bacigalupo *et al.*, 2020) electrical transport (Neiman *et al.*, 2005) and vibration dynamics (Yi *et al.*, 2017) areas. In the field of EM materials, the term was first coined by Zhu *et al.* through achieving a negative permittivity nanocomposite by coating a homogeneous layer of conductive polypyrrole (PPy) on the surface of WO_3 nanoparticles (NPs) (Zhu *et al.*, 2010). Several other dielectric and magnetic fillers in 0D, 1D or 2D forms were introduced in functional polymeric matrices (Fig. 1) to generate metacomposites. However, the obtained EM functionality is tarnished by additional mechanical or chemical treatments required to ensure homogeneous microstructure as well as strong filler/matrix bonding. Hence, despite all these previous works the term metacomposite has yet to be explicitly and properly defined. Here, a metacomposite is defined as a composite material that takes its properties from both the composite fillers as functional units and their prescribed ordered structure at single or multiple length scales. It is further elucidated as follows: (1) a composite material featured with metamaterial characteristics via incorporating functional fillers into the matrix, constituting a true piece of composite material rather than a mere structure; (2) ultimate EM properties would not only depend on the filler intrinsic properties but also on their much-simplified topology as opposed to conventional metamaterials; (3) commonly composite manufacturing technologies could be implemented to economically improve metacomposite processing. Meanwhile, in view of the emerging trends in electronic devices, fillers should still have fine size in favor of device miniaturization and possess high and flexible response towards EM waves. We and several other research groups have established that ferromagnetic microwires endow multifunctional polymer-based composites with merits such as low filler content, high field/stress sensitivity, bias-free DNG feature and excellent mechanical properties (Qin and Peng, 2013; Makhnovskiy *et al.*, 2008; Panina *et al.*, 2009; Makhnovskiy *et al.*, 2006; Ipatov *et al.*, 2009). Therefore, an easily manufactured and versatile composite enabled by ferromagnetic microwires is introduced to the metacomposite landscape which is the main focus of the present chapter. The remainder of the chapter is organized as follows: “Design Fundamentals of Microwire Metacomposites” provides the essential concepts on microwire metacomposite design. “Optimization of Microwire Metacomposites” reviews recent advances in the optimization of microwave properties of metacomposites incorporating ferromagnetic microwires. “Manufacturing and Application Prospects of Microwire Metacomposites” is devoted to the manufacturing and application perspectives of microwire metacomposites. Finally, the main conclusions and prospects are summarized in “Summary and Outlook”.

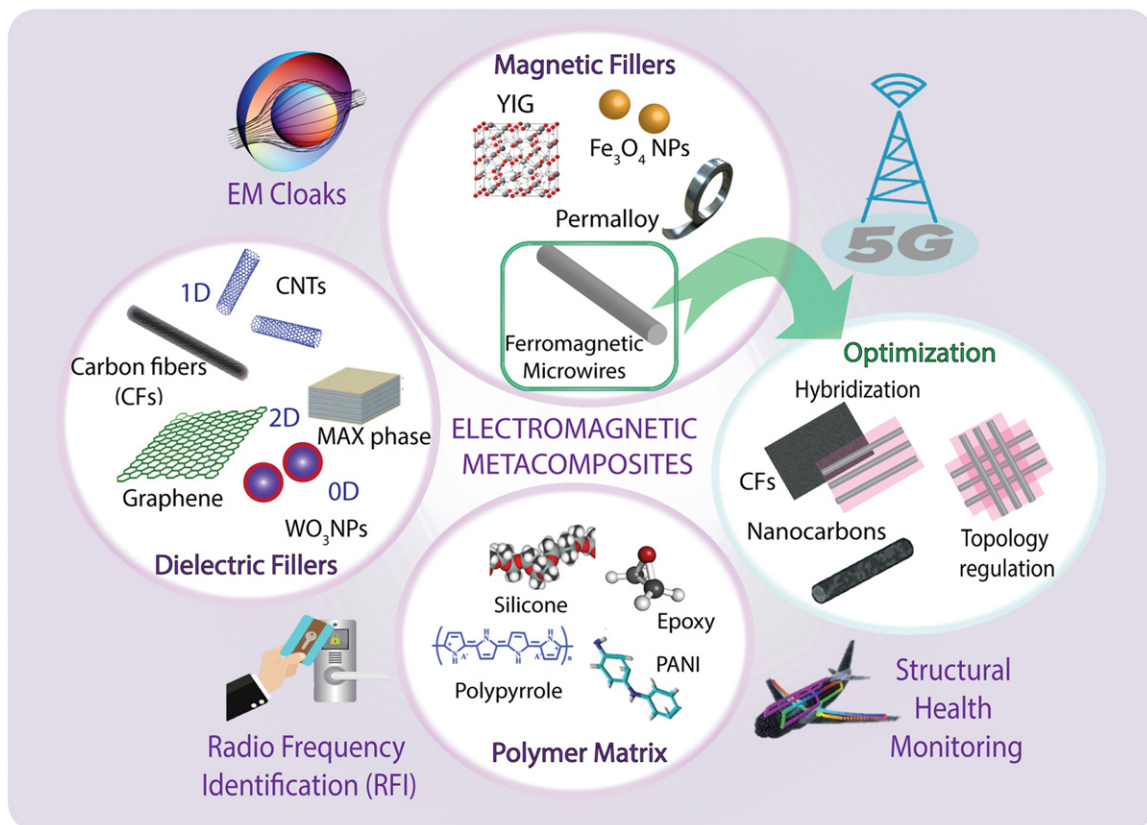


Fig. 1 Summary of polymer-based metacomposites containing dielectric and magnetic fillers. A new member is introduced to the metacomposite family enabled by ferromagnetic microwires which optimization and prospective applications will be discussed in the present chapter.

Design Fundamentals of Microwire Metacomposites

Maxwell's equations can be transformed from microscopic to macroscopic form enabling to describe the EM response of a metamaterial based on ϵ and μ as long as the size of the building blocks is within the order or much smaller than the wavelength (Sihvola, 2007). At the subwavelength scale, both parameters can be independently manipulated to obtain a media with either single negative ϵ (ENG), single negative μ (MNG) or both negative (DNG), thanks to the decoupling of electric and magnetic field. In this section, we will first discuss the theoretical background of obtaining negative ϵ and μ . Next, we will focus on the capability of microwires to realize metamaterial features and their incorporation in functional polymer matrix to enable metacomposites.

Complex Permittivity and Permeability

Negative permittivity

Materials demonstrating negative ϵ can be found in nature. The Drude model describes the EM excitation from elementary building blocks as a response from plasmons (collective oscillation of electron gas density) (Cheng *et al.*, 2019). The characteristic frequency indicating the equilibrium where such excitation occurs is expressed as (Cheng *et al.*, 2019):

$$\omega_p = \sqrt{\frac{n_{\text{eff}} e^2}{m_{\text{eff}} \epsilon_0}} \quad (1)$$

where $\omega_p = 2\pi f_p$ and f_p represents the plasma frequency, n_{eff} the effective concentration of diluted electrons, m_{eff} the effective weight of electron and e is electron charge (1.6×10^{-19} C).

In turn, the effective permittivity function takes the following form on the interaction with electromagnetic wave:

$$\epsilon_r = 1 - \frac{\omega_p^2}{\omega^2 + \omega_D^2} \quad (2)$$

where ω is angular frequency and the parameter ω_D represents the damping frequency.

The effective permittivity is negative below f_p as long as the losses are small. Therefore, obtaining negative permittivity is reduced to the design of the plasma frequency. From Eq. (1), f_p depends on n_{eff} and m_{eff} which in turn are linked to the building blocks dimensions. In the case of metacomposites containing nanoscale fillers, f_p is relevant to their volume fraction and distribution in the matrix. The higher the f_p , the larger the amount of filler derived from the higher electron concentration. When it comes to metacomposites containing very thin metallic wires (of the order of few microns), the f_p and ϵ can be deduced as per Pendry's work (Pendry *et al.*, 1996):

$$f_p^2 = \frac{c^2}{2\pi b^2 \ln(\frac{b}{a})} \quad (3)$$

$$\epsilon_r = 1 - \frac{\omega_p^2}{\omega \left(\omega + i \frac{\epsilon_0 b^2 \omega_p^2}{\sigma \pi a^2} \right)} \quad (4)$$

where a , b and c are wire radius, wire periodicity and speed of light (3×10^8 m/s), respectively. σ represents the conductivity of the wires.

Thus, a very simple configuration of a regular array of thin wires has enormous implications in acquiring negative permittivity. By adjusting the distance between the wires and selecting adequate wire diameter, f_p can be modulated and designed at microwave frequencies. The dielectric response in this case is also free of filler aggregation which is often an issue in nano-composite fabrication. Therefore, the wire medium is an efficient functional filler to achieve negative ϵ in metacomposites.

Negative permeability

Compared to negative permittivity, a negative permeability is more difficult to acquire in natural materials. Negative μ is induced in some ferrimagnetic or dielectric materials due to the current loops of quasi-conductive networks which generate weak magnetic response and thus rendering no practical value (Shi *et al.*, 2012). On the other hand, ferromagnetic materials can be selected as functional fillers to generate negative permeability where the ferromagnetic resonance (FMR) takes place (Pimenov *et al.*, 2005). Moreover, FMR frequency can be easily tuned by external magnetic fields which makes ferromagnetic inclusions ideal fillers to access DNG features taking into account the above f_p theory. In the case of ferromagnetic microwires, the effective μ can be described as (Liberal *et al.*, 2011):

$$\mu_{\text{eff}} = 1 + \frac{\mu_0 \gamma M_s (\mu_0 \gamma H_0 - j\omega\alpha)}{-\omega^2 + \omega_{\text{FMR}}^2 - j\omega\alpha\mu_0 \gamma (2H_0 + M_s)} \quad (5)$$

$$\omega_{\text{FMR}} = \mu_0 \gamma \sqrt{(H_0 + M_s) H_0} \quad (6)$$

$$H_0 = H_{\text{DC}} + H_k \quad (7)$$

where μ_0 and μ_{eff} are the vacuum and effective permeability, M_s is the saturation magnetization, H_{dc} and H_k are external and anisotropic magnetic fields, $\omega_{\text{FMR}} = 2\pi f_{\text{FMR}}$ with f_{FMR} as the FMR frequency, γ is the gyromagnetic ratio and α is the damping

factor. With such parallel arrangement, not only negative μ is achieved by modulating properties such as H_k and M_s during the wire fabrication, but also negative ϵ can be designed by fulling the plasmonic behavior in the wire medium.

Double negative, ϵ and μ

As an example of DNG design of microwire metacomposites, Fig. 2 shows the calculated ϵ and μ of a parallel array of microwires embedded into a polymer matrix. A wire diameter of $16.6 \mu\text{m}$ and a wire spacing of $b = 10 \text{ mm}$ were used to calculate ϵ by Eq. (4) whereas $\gamma = 1.93 \times 10^{11} \text{ T}^{-1}$, $H_{\text{DC}} = 300 \text{ Oe}$ and $M_s = 828 \text{ Gs}$ determined the permeability through Eq. (5). For convenience, the microwave response of the polymer matrix was ignored. It is clearly observed that in the frequency band of 2.4–4.5 GHz, a DNG feature is identified. Such DNG region is “moveable” by applying moderate magnetic field to modulate the frequency range of negative permeability. Meanwhile, through adjusting wire spacing the plasma frequency and thus the region of negative permittivity can be also modulated. Left-handed properties in metacomposites are thus reduced to the topological design at the meso-/macro-scale and the design of the filler properties at the micro-scale.

Characteristics of Microwire Metacomposites

Ferromagnetic microwires have been extensively studied for decades due to their exceptional sensing and EM properties owing to their distinguished giant magneto/stress impedance effect and soft magnetic properties (Phan and Peng, 2008). The capability of microwires to realize metamaterial features was also demonstrated in the case of a single wire. Labrador *et al.* (2010) explored the left-handed characteristics of an Fe-rich glass-coated microwire employing a rectangular waveguide in the X band. Inside the rectangular waveguide, the microwire was placed on Rohacell foam slices and oriented parallel to the incident electric field and perpendicular to the magnetic field. Negative permeability originated from the natural FMR and the negative permittivity resulted from the interaction of the microwires with the metallic rectangular waveguide. The electrically isolated microwire behaved as capacitive-loaded inducing negative permittivity values while the natural FMR occurring without magnetic field greatly simplified the structure. Moreover, application of a magnetic field could enable the design of magnetotunable left-handed systems

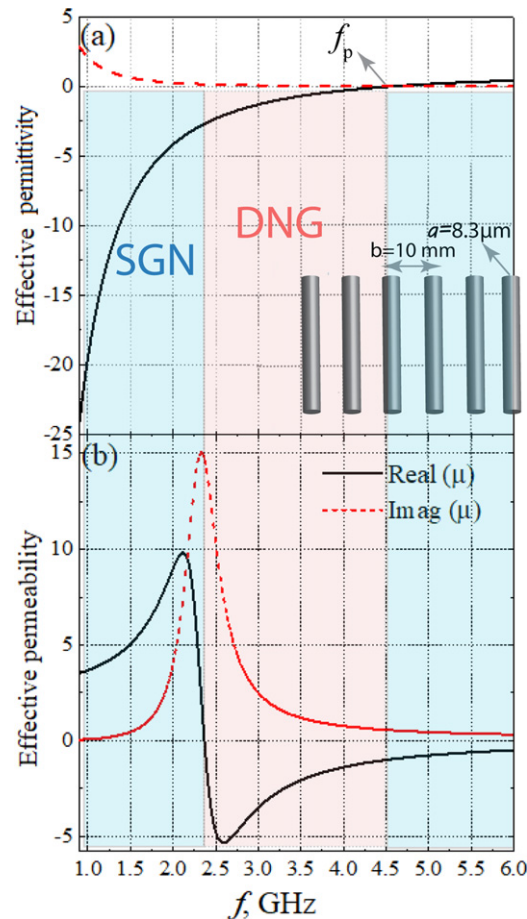


Fig. 2 Theoretical calculations of frequency plots of (a) permittivity and (b) permeability of a wire medium consisting of periodically arranged glass-coated $\text{Fe}_{77}\text{Si}_{10}\text{B}_{10}\text{C}_3$ microwires. The inset depicts that the structure has a periodicity b of 10 mm. Double negative (DNG) feature is identified in the frequency range of 2.4–4.5 GHz.

with wide-frequency band. García-Miquel *et al.* (2009) further demonstrated the ability of microwires to realize left-handed properties in an array of two layers of three CoSiB wires, 2–3 μm in diameter. The DNG condition was demonstrated by the rise of transmission with the DC magnetic field. Liu *et al.* (2008) also developed a metamaterial configuration by combining long conductive fibers along the electric field and microwires along the magnetic field.

The above results demonstrate that such versatile fine element is a very competitive material for constituting metacomposites. By employing microwires in a periodical fashion and incorporating them in polymer matrix, metamaterial features can be realized. Most importantly, this design makes metacomposites a true piece of material which is of great engineering significance. For the fabrication of microwires-enabled metacomposites, we adopt conventional hand lay-up and autoclave curing, which is recognized as a reliable polymer-based composites manufacturing for commercial production. The wire-metacomposites can be designed based on the intrinsic properties of wires and mesostructural parameters such as wire spacing. This offers a much easier platform for manipulating EM properties compared to the aforementioned conventional metacomposites susceptible to synthesis conditions. Taking advantage of the natural FMR occurring in Fe-based microwires and their cost-efficiency, $\text{Fe}_{77}\text{Si}_{10}\text{B}_{10}\text{C}_3$ microwires were aligned with 3, 7 and 10 mm spacing in 950 E-glass prepregs, followed by a standard curing procedure to realize a simple configuration of parallel wire-metacomposites (Fig. 3) (Luo *et al.*, 2013). The microwave behavior was tested by free-space technique in the 0.9–17 GHz under DC magnetic bias up to 3 kA/m.

From Fig. 4, transmission windows are clearly identified in the frequency range of 1–7 GHz of the metacomposite with 3 mm wire spacing (Luo *et al.*, 2013) indicating that negative ϵ and a negative μ are simultaneously obtained. Negative ϵ below f_p derived from the parallel alignment of wires (Pendry *et al.*, 1996) while negative μ resulted from the FMR of wires (García-Miquel *et al.*, 2009). Moreover, such transmission window is excited without external magnetic field originating a natural DNG feature which offers a great advantage over meta-structure consisting of Co-based wires where DNG characteristics emerge with burden magnets (Luo *et al.*, 2014a). This enables the application of such metacomposites in compact devices and lightweight structures.

However, with increasing magnetic field, the shifting of transmission windows is negligible. Since microwires are very heat- and stress-sensitive (Wang *et al.*, 2011; Qin *et al.*, 2013) the applied curing cycle (i.e., 125°C heating for 2 h and 0.62 MPa for 4.5 h) (Panina *et al.*, 2009) would have greatly changed the stress distribution in the wires resulting in the formation of magnetically hard crystallites on the surface. Such crystallites dramatically degrade the microwire magnetic properties (Wang *et al.*, 2012) suppressing the expected shifts in transmission windows. Another phenomenon is the f_p discrepancy between the experimental data and calculated values. From Eq. (3), f_p of 4.8, 6.6 and 16.6 GHz are obtained for composites with wire spacing of 10, 7 and 3 mm,

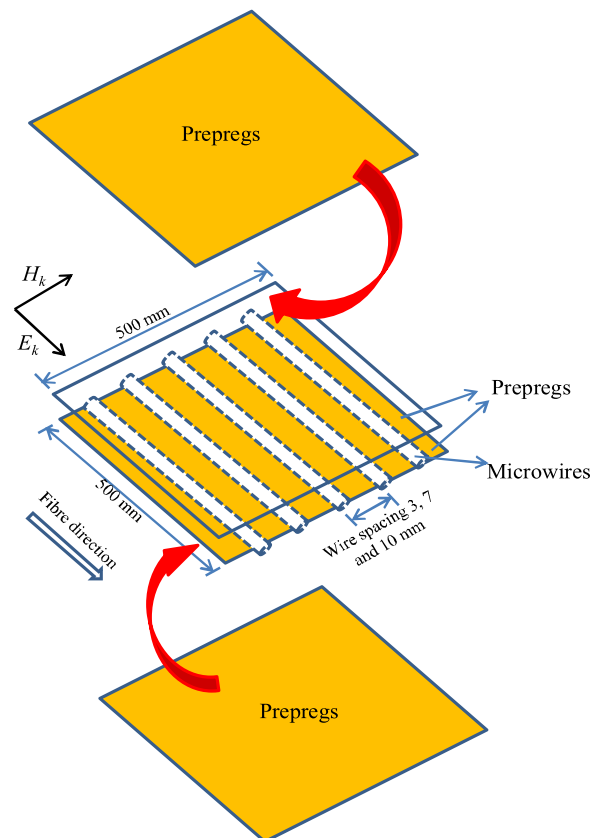


Fig. 3 Schematic illustration of the process for manufacturing composites containing Fe-based microwires in a parallel manner with wire spacing of $b = 3, 7$ and 10 mm. Reprinted from Luo, Y., Peng, H.X., Qin, F.X., *et al.*, 2013. Fe-based ferromagnetic microwires enabled meta-composites. Appl. Phys. Lett. 103, 1–5. Available at: <https://doi.org/10.1063/1.4850196>. With the permission of AIP Publishing.

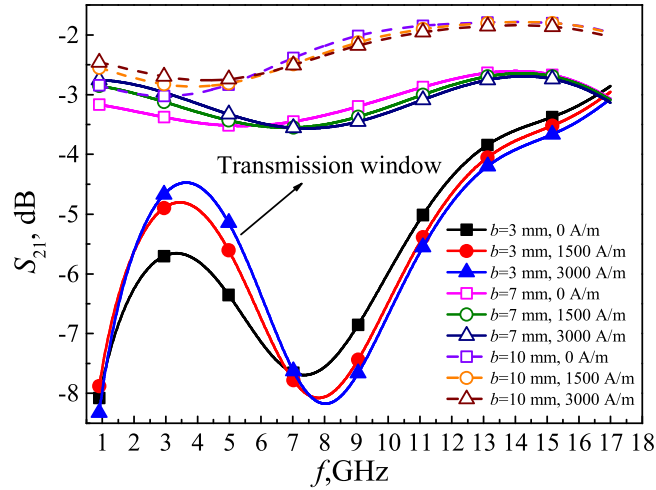


Fig. 4 Frequency dependencies of transmission (S_{21}) coefficients of parallel microwire composites with different wire spacing, $b = 3, 7$ and 10 mm, respectively. Reprinted from Luo, Y., Peng, H.X., Qin, F.X., *et al.*, 2013. Fe-based ferromagnetic microwires enabled meta-composites. Appl. Phys. Lett. 103, 1–5. Available at: <https://doi.org/10.1063/1.4850196Y>. With the permission of AIP Publishing.

respectively. Experimentally, when the wire spacing is larger than 3 mm, f_p exhibits much lower values i.e., 1.4 GHz for $b = 10$ mm and 1.6 GHz for $b = 7$ mm (Fig. 5). Considering that the main contribution to ϵ in ferromagnetic microwires comes from the outer shell of their domain structure (Luo *et al.*, 2013) the actual interaction area with microwaves is significantly reduced for Fe-based wires which outer shell domain only occupies a trivial portion (Phan and Peng, 2008). Thus, an effective diameter a_{eff} must be introduced in Eq. (3) to account for such equivalent area (Luo *et al.*, 2013):

$$f_p^2 = \frac{c^2}{2\pi b^2 \ln\left(\frac{b}{a_{eff}}\right)} \quad (8)$$

Since $a_{eff} \leq a$, the f_p is significantly compromised, resulting in the disappearance of DNG feature for wire spacing larger than 3 mm. A sudden increase in f_p is observed when the spacing is decreased to 3 mm. Dynamic wire-wire wave interactions occur in such closely packed microwires and have essentially compensated the excited circumferential magnetic fields hence the a_{eff} . Meanwhile, 7 mm or 10 mm spacing are too wide to induce interactions with microwaves (Velázquez *et al.*, 1996, 1999).

Albeit double negative indices were obtained in such a simple configuration of parallel wire composites, the transmission level is not promising due to the loss generated by the wires. Moreover, the reflection level is relatively high in e.g., 3 mm spaced wire array due to high wire content and the DNG feature is obtained in a rather narrow band. Thus, further optimization approaches based on wire intrinsic properties, wire topological configuration or the incorporation of other functional fillers into the meta-composite structure may be applied for modulating magnitude and frequency band of left-handed features. This will be the focus of our next section.

Optimization of Microwire Metacomposites

A truly versatile metacomposite should be developed using functional fibers optimized to achieve a variety of superior functions. Within this framework, we will discuss the main aspects in the design optimization of microwire metacomposites such as properties of the microwires themselves, topological factors and hybridization with other functional fillers. We will also explore the accomplished tunability of such metacomposites by external stimuli (magnetic/electric field and mechanical stress).

Meso and Micro-Structural Modulation

Wire length and diameter

The length of the microwires affects their dispersion in the matrix. If the wires are too long a good dispersion in the matrix will be challenging. On the other hand, if the wires are too short the demagnetization effect is so strong that ruins the overall EM response of the metacomposites. The length will also influence the profile of the effective permittivity (Panina *et al.*, 2011a). Short pieces of microwires are characterized by a permittivity of resonance type or Lorentz dispersion as the wires behave as dipole antennas with the resonance at half-wave length condition (Panina *et al.*, 2011a):

$$f_{dres} = \frac{c}{2l\sqrt{\epsilon_m}} \quad (9)$$

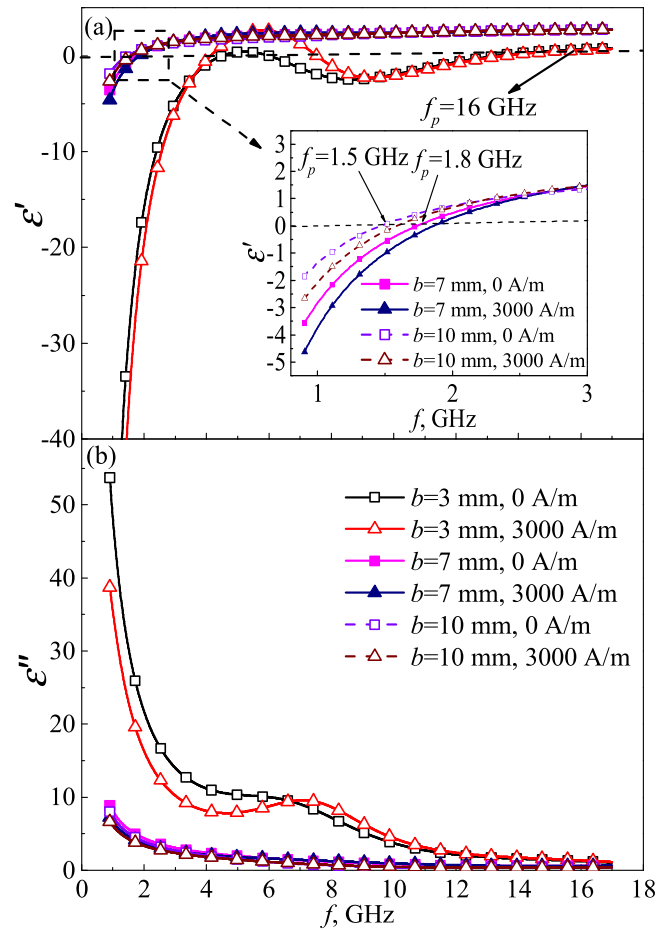


Fig. 5 Frequency dependencies of real and imaginary part of effective permittivity of microwire composites with different wire spacing, $b = 3, 7$ and 10 mm, respectively. The insets show the enlarged real part of effective permittivity in frequency band of $0.7\text{--}3$ GHz. Reprinted from Luo, Y., Peng, H.X., Qin, F.X., *et al.*, 2013. Fe-based ferromagnetic microwires enabled meta-composites. *Appl. Phys. Lett.* 103, 1–5. Available at: <https://doi.org/10.1063/1.4850196Y>. With the permission from AIP Publishing.

where l corresponds to wire length and ϵ_m is the permittivity of the matrix. For this system, the real part of permittivity becomes negative in a frequency band beyond the resonance and the wave propagation will be restricted in this frequency range. Otherwise, if the relaxation in the system is large, the real part of permittivity remains positive. For composites incorporating long continuous microwires, the dispersion of the effective permittivity corresponds to that of a diluted plasma or Drude dispersion with negative value of the real part below the plasma frequency. In this case, the system is well described by Eqs. 3 and 4.

With respect to wire diameter, at a given glass coating thickness the magnetoimpedance effect is improved with increasing wire radius (Qin *et al.*, 2010a). This enables composites incorporating microwires with large radius to exhibit higher field tunability than those with smaller radius. The dielectric response of such composites is also stronger. Thinner wires tend to present weaker field effects due to their much stronger skin effect. An important consideration for realizing metamaterial feature at microwave frequency is that the microwire diameter should be comparable to the skin depth, as too large diameter will cause huge reflection (Pendry *et al.*, 1996; Panina *et al.*, 2011b). Although it is still possible to penetrate into most of the inner core of Fe-based wire or the outer shell of Co-based wire, submicron wires or nanowires would be the ideal case (Qin and Peng, 2013). However, reducing the wire diameter will reduce the volume fraction of wires and hence the permittivity and permeability. Panina *et al.* (2011b) revealed that the wire radius has a profound impact on the intensity of transmission S_{21} but much less effect on its tunability. Qin *et al.* (2012b) also confirmed that the wire geometry and hence, the plasma frequency control the patterns of scattering spectra.

Wire composition

Excellent soft magnetic properties, which depend mainly on wire composition, would be preferable to realize strong field tunable effect in the metacomposites. Magnetic softness indicates larger dynamic magnetic permeability and thus larger relaxation parameter (Qin *et al.*, 2012b). These properties should be controlled during the fabrication of the microwires and optimized further with post-fabrication treatments such as current annealing before their incorporation in the composite.

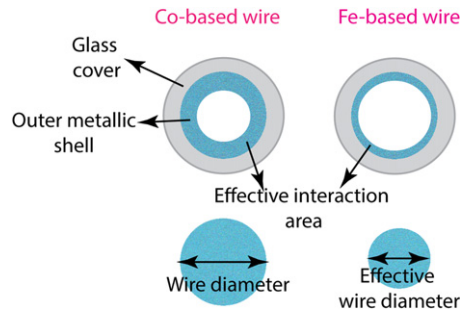


Fig. 6 Schematic of microwave interaction area of Co-based and Fe-based microwires. The effective diameter accounts for the equivalent area of Fe-based microwires.

In terms of microwire selection, two categories are generally considered: Co-based and Fe-based. Co-based microwires realize DNG feature from their superior magnetoimpedance properties over their Fe-based counterparts and nearly zero magnetostriction attributed to their circumferential anisotropy (Carbonell *et al.*, 2010). Fe-based microwires, on the other hand, have positive magnetostriction and thus significantly different domain structure consisting of an inner axially magnetized single domain and an outer shell with radial magnetization direction. As a consequence, their static and dynamic EM responses are also distinct from those of Co-based wires (Vazquez and Adenot-Engelvin, 2009). Besides, as aforementioned, the natural FMR of Fe-based wires facilitates negative permeability without the assistance of external fields creating additional degrees of freedom in DNG design. Last but not least, Fe-based microwires are much cheaper compared to Co-based microwires which make them desirable for practical applications.

The composition of the wires also determines the prediction of the plasma frequency of the metacomposites. As shown in section “Characteristics of Microwire Metacomposites”, Eq. (3) failed to predict f_p in composites incorporating Fe-based microwires arranged at certain spacing. Dielectric response of ferromagnetic wires is controlled through modifying plasmons on the surface by creating circumferential magnetic fields. Thus, the dielectric response to microwave energy mainly comes from the outer shell domain of wires (Luo *et al.*, 2013). The outer shell of Fe-based wires constitutes a rather trivial portion of the whole wire volume (Phan and Peng, 2008) and thus the effective wave-matter interaction area is dramatically reduced (Fig. 6). Consequently, an “effective diameter” (Fig. 6) must be taken into account to describe the equivalent interaction area as mentioned above. On the other hand, Co-based wires possess domain structure with large volume of circular outer shell (Phan and Peng, 2008) and the “effective diameter” would be only a touch smaller than the real wire diameter, rendering f_p closer to the calculated theoretical value (Luo *et al.*, 2013).

Wire arrangement

One issue with parallel wire metacomposites (“Characteristics of Microwire Metacomposites”) is their high reflection due to large wire content in e.g., 3 mm spacing. A simple approach to address this issue is to alter the wire topology bearing in mind that simple structure is always of primary concern. Liu *et al.* (2008) theoretically demonstrated that an orthogonal array incorporating ferromagnetic microwires and carbon fibers results in DNG characteristics. Owing to the salient microwave properties of Fe-based wires, using microwires alone for constructing an orthogonal structure would be a better choice to obtain DNG features.

Orthogonal wire metacomposites are presented in Fig. 7 (Luo *et al.*, 2014b) fabricated by a similar curing protocol to that of parallel metacomposites. The composites were also characterized by free space technique with the electrical component (E_k) perpendicular to the glass fibers of the polymer (Fig. 7). The horizontal microwires can be regarded as a typical wire medium for inducing negative permittivity while the vertical wires can be considered as shortcut parallel wires between neighboring continuous wires. Remarkably, transmission windows emerge in the range of 1–6 GHz for the metacomposite with 10 mm spaced orthogonal arrays (Fig. 8). Since orthogonal metacomposites incorporate significantly less wires but demonstrate a larger wave transparency than metacomposites containing parallel wires (Fig. 4), such configuration would be better for miniaturized cloaking devices. The orthogonal structure with 3 mm spaced wires also shows a slightly higher transmission level than the 3 mm parallel wire metacomposites. The improvement in transmission is attributed to the vertical wire array perpendicular to the electrical component of the incident wave. The perpendicular wires also improve ϵ due to their small axial component along E_k which generates circumferential magnetic fields that also enhances μ (Kraus *et al.*, 2013). An extra contribution to permeability comes also from the weak interaction between the vertical wires and the magnetic component (H_k) of incident waves (Vazquez and Adenot-Engelvin, 2009). Therefore, the transmission is facilitated by the improved impedance match according to $Z = (\mu/\epsilon)^{1/2}$. Furthermore, the transmittance could be optimized through tuning the amount of inserted vertical wire arrays which is instrumental for developing cloaking devices. Overall, the orthogonal configuration has a better transmission performance but less filler inclusion compared with parallel wire configuration.

However, tuning the observed transmission windows of both parallel and orthogonal metacomposites is still a tricky issue which is a disadvantage when it comes to the development of multiband and/or tunable metamaterials. Beyond magnetic-stimuli manipulation of the metacomposite functionalities, Uddin *et al.* (2019, 2020) proposed to program the EM responses by designing the wire functional units and assembling them in a specific arrangement. The programming was based on wire content and periodicity as well as the arrangement of microstructurally modulated Co-based microwires (as-cast (A) and current annealed

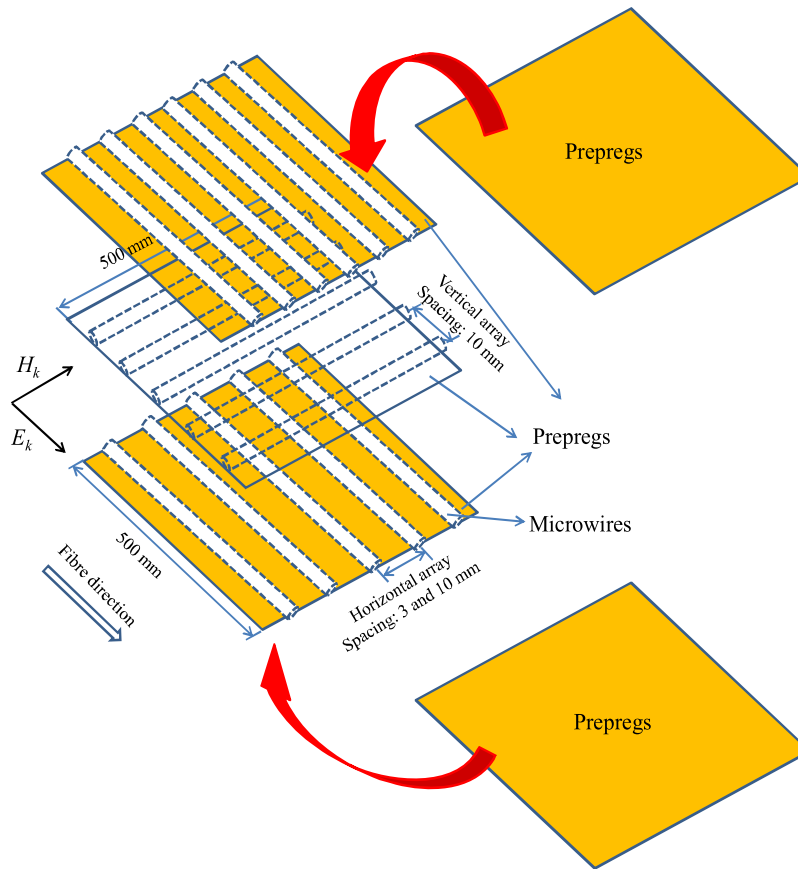


Fig. 7 Schematic view of the manufacturing process of an orthogonal wire array metacomposite with a fixed wire spacing of 10 mm perpendicular to glass fibers and different horizontal wire spacings of 3 and 10 mm. Reprinted from Luo, Y., Peng, H.X., Qin, F.X., *et al.*, 2014b. Metacomposite characteristics and their influential factors of polymer composites containing orthogonal ferromagnetic microwire arrays. J. Appl. Phys. 115, 1–6. Available at: <https://doi.org/10.1063/1.4874176Y>. With permission from AIP Publishing.

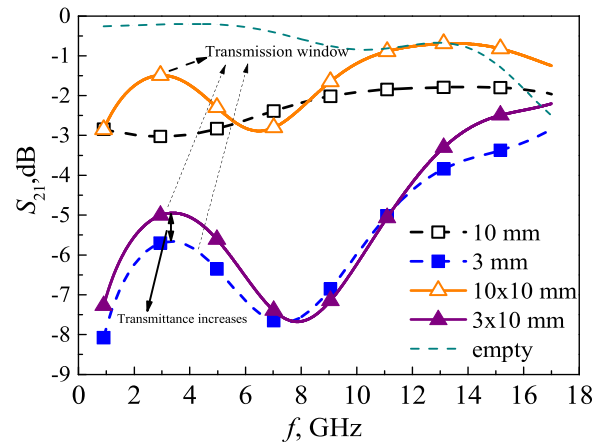


Fig. 8 Frequency plots of transmission spectra of polymer composites with parallel and orthogonal wire arrays and a blank composite (with no wires) with E_k along the glass fibers in the absence of external fields. Reprinted from Luo, Y., Peng, H.X., Qin, F.X., *et al.*, 2014b. Metacomposite characteristics and their influential factors of polymer composites containing orthogonal ferromagnetic microwire arrays. J. Appl. Phys. 115, 1–6. Available at: <https://doi.org/10.1063/1.4874176Y>. With permission from AIP Publishing.

(X: B = 30 mA or C = 40 mA)) in the array (**Fig. 9**). The microwave behavior was examined with a Rohde & Schwarz ZNB 40 vector network analyzer (VNA) by using a WR-90 waveguide in TE₁₀ dominant mode. Related fabrication and microwave characterization details can be found elsewhere (Uddin *et al.*, 2020).

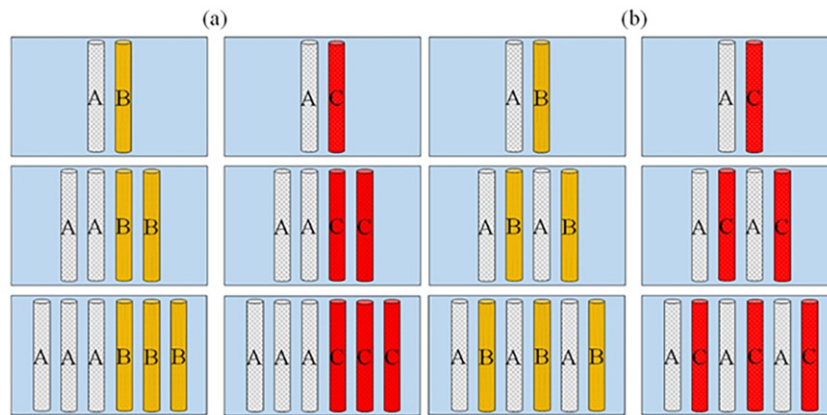


Fig. 9 Arrangement of Co-based microwires in the composite (a) in a repetitive pattern and (b) in an alternating pattern. A, B, and C correspond to as-cast, 30 mA and 40 mA annealed microwires, respectively. The spacing between the wires was varied from 2 mm to 1 mm. Reprinted from Uddin, A., Estevez, D., Qin, F.X., Peng, H.X., 2020. Programmable microwire composites: From functional units to material design. *J. Phys. D Appl. Phys.* 53, 155302. Available at: <https://doi.org/10.1088/1361-6463/ab6ccd>. With permission from IOP Publishing.

Fig. 10 shows the transmission spectra for composites with as-cast and annealed microwires arranged in several combinations with 2 mm and 1 mm spacing between them. Increasing the number of wires in the AX (**Fig. 10**(d) and (e)) and AAXX arrays (**Fig. 10** (b) and (c)) where X represents either 30 or 40 mA annealed wires, results in a blueshift of the transmission dip frequency regardless of wire spacing. Such frequency relates to the Lorentz-type dielectric resonance or dipolar behavior of the short-cut wires in the waveguide (Eq. (9)). Gradually replacing B wire by C leads to a redshift of the transmission dip frequency. A marked redshift is also noticed when decreasing the wire periodicity from 2 to 1 mm.

The above variations in the transmission spectra of the composites depend on two main effects: the change in conductivity of the arrays and the wire-wire magnetic interaction. Increasing the wire content enlarges the total cross-sectional area, diminishing the total resistivity and strengthening the skin effect. The conductivity of the array is also altered due to the difference in conductivity between the wires (larger for annealed wires). With respect to the effect of wire periodicity, decreasing the inter-wire distance redshifted the resonance due to stronger inter-wire coupling and more efficient wave propagation within the wire array (Uddin *et al.*, 2020). Hence, modulating the individual properties of each resonant microwire collectively facilitated the control of EM response of the metacomposite. Rather than focusing mainly on structure/performance relationship, such programming strategy paves the way to realize EM functions based on the concept of ordered structures and functional units themselves. Moreover, it also inspires the development of active frequency selective surfaces based on microwire metacomposites.

Plainification

In the previous section, viable approaches to program wave scattering in microwire metacomposites based on microstructural and topological modulation were presented. Although such methods enabled the modulation of scattering properties to a large extent, strategies other than increasing wire content must be explored to simplify further the design/manufacture and avoid structural disintegrality. In this context, the concept of “plainification” could be applied in which the metacomposite design fully exploits its structure through interface engineering while maintaining the same filler content (Li *et al.*, 2019). Such concept has been implemented for structural adjustment of porous graphene oxide (GO) aerogels to tune the complex permittivity and develop highly efficient EM wave absorbers (Zhang *et al.*, 2020a,b). Alloys have also exploited such approach by altering grain boundaries with fewer or even zero alloying elements (Li and Lu, 2019; Zhao *et al.*, 2019). We have also demonstrated the potential of plainification by designing vertical interfaces on carbon nanocomposites to trigger modulation of microwave dielectric properties (Li *et al.*, 2019). On the other hand, randomly dispersed or so-called intrinsic/random metacomposites where functional fillers are randomly distributed in an insulating matrix have been investigated by Xie *et al.* (2018, 2017). In such composites, the size of the filler is no longer dependent on wavelength because the DNG feature directly originates from the intrinsic property of building blocks (Shi *et al.*, 2012). Inspired by these works, we move forward to extrapolate the plainification design by in-built vertical interfaces in randomly dispersed microwire metacomposites (Uddin *et al.*, 2021). Two kinds of metacomposites were prepared. The first type incorporating the same type of wire, i.e., as-cast A, 30 mA-current annealed B or 40 mA-current annealed C (**Fig. 11**(a)). The second type of composite corresponds to incorporating as-cast A and annealed short-cut wires X (where X corresponds to B or C annealed wires) in separate regions with variable proportions while keeping the same overall filler content (50 short-cut wires) (**Fig. 11**(b)).

Firstly, by incorporating the same type of microwires and modifying their microstructure through current annealing, additional fillers are avoided. Secondly, by separating the randomly distributed as-cast and annealed wires in two regions, an extra factor comes into play, i.e., interface-induced polarization. This polarization relates to the difference in conductivity, permittivity and

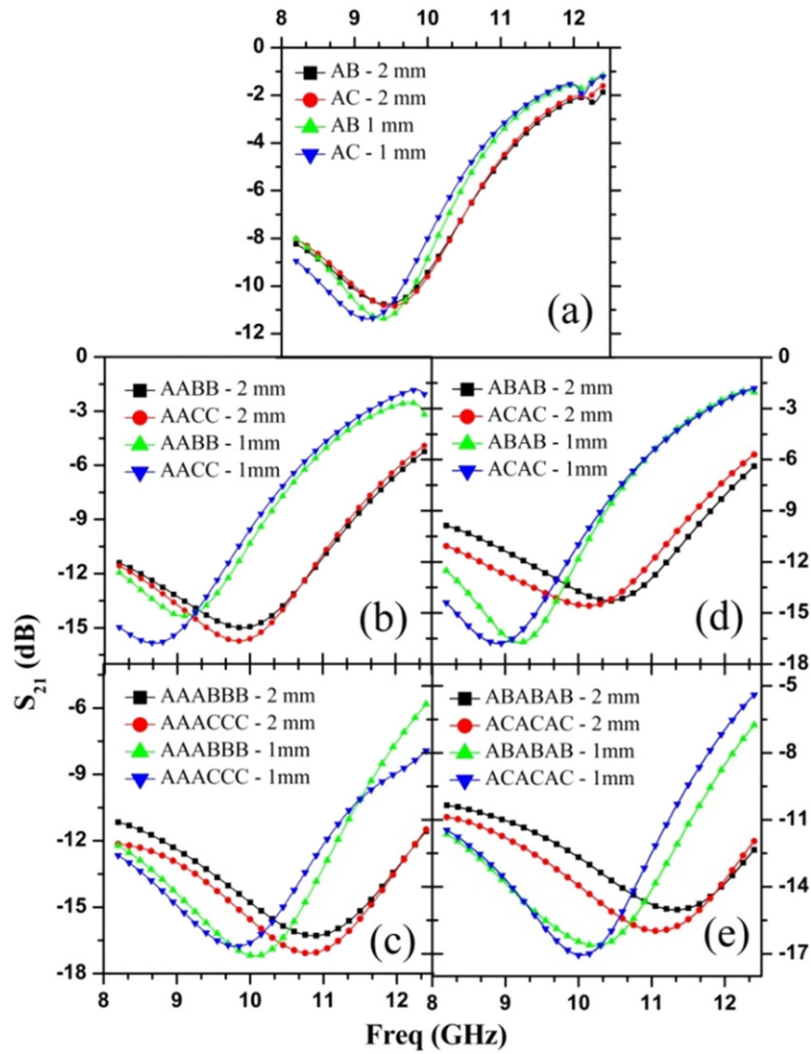


Fig. 10 Frequency dependence of transmission coefficient- S_{21} for composites containing different combinations of as-cast, 30 and 40 mA-annealed wires as a function of number of wires and inter-wire spacing. A corresponds to as-cast wires; B and C correspond to 30 mA and 40 mA current annealed wires, respectively. Reprinted from Uddin, A., Estevez, D., Qin, F.X., Peng, H.X., 2020. Programmable microwire composites: From functional units to material design. *J. Phys. D Appl. Phys.* 53, 155302. Available at: <https://doi.org/10.1088/1361-6463/ab6ccd>. With permission from IOP Publishing.

relaxation time of charge carriers across the in-built vertical interface (Li *et al.*, 2019). Thirdly, by altering one of those regions through variations in the corresponding wire volume concentration, the scattering properties could be manipulated to a great extent. These three approaches are sufficient to provide a broad tunability of the transmission spectra of microwire meta-composites, as will be elucidated next.

Effect of the introduced interfacial region

Fig. 12 presents the scattering properties of the composites incorporating randomly distributed microwires of the same type and a combination of as-cast and annealed wires separated by an interfacial region (Uddin *et al.*, 2021). A passband extending from 8.5 to 11 GHz appears in the transmission spectrum of composites containing as-cast wires A (Fig. 12(a)) which converts into transmission dips or stopbands for the composites with annealed wires B and C. Band-stop filters block signals that lie between the two cut-off frequencies (f_L and f_H) but pass all those either side of this range. The additional resonances seen for the composites containing the B wires originate from the overlapping of wires within the polymer matrix which also lowers the resonance frequency. When the interfacial region is introduced into the composites containing equal loading of as-cast A and annealed wires X (Fig. 12(d)), two transmission windows are observed together with dips in reflection and absorption spectra (Fig. 12(d)–(f)). The two transmission windows originate from each separate region and their coexistence in the composite. Differences in conductivity and permittivity between the two regions generate charge accumulation in the vertical interface under the electric field influencing the overall dielectric properties and hence the EM response. In addition, the transmission spectrum blueshifts almost as a single unit with lower amplitude

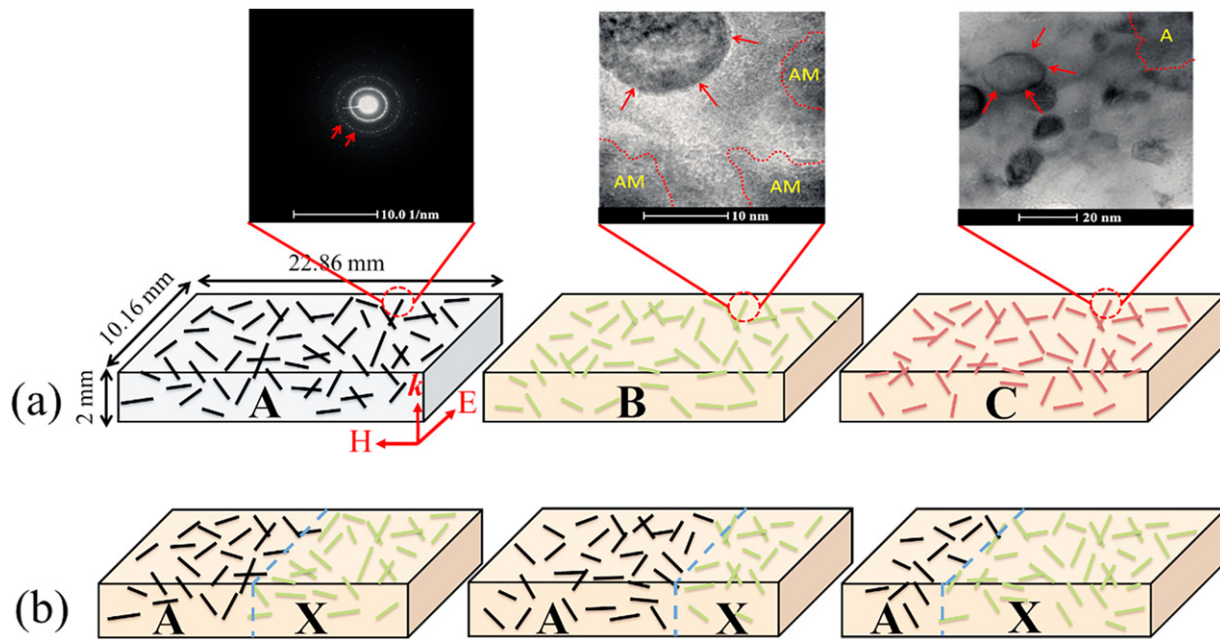


Fig. 11 Randomly dispersed short-cut microwire composites. (a) Composites incorporating the same type of wire, as-cast A, 30 mA-annealed B or 40 mA-annealed C with a total wire amount of 0.053 vol% (50 wires). The SAED patterns HRTEM images in the insets show the nanocrystalline feature of the microwires, where “AM” corresponds to amorphous phase; (b) Composites combining the as-cast A and annealed wires X (B or C annealed wires) in separate regions and different proportions. The dotted line represents the vertical interface formed between the two regions. Reprinted from Uddin, A., Qin, F.X., Estevez, D., Peng, H.X., 2021. Vertical interface augmented tunability of scattering spectra in ferromagnetic microwire/silicone rubber metacomposites. *EPJ Appl. Metamater.* 8. Available at: <https://doi.org/10.1051/epjam/2021003A>. With permission from EDP Sciences.

as the 30 mA annealed wires (B) are replaced by the 40 mA annealed wires (C). Such changes correlate to the gradual relief of internal stresses and structural relaxation experienced during the annealing process of the wire.

Effect of shifting the interfacial region

Here, the scattering response of the composites will be modified by moving one region of the sample relative to another through variation in wire volume fraction (Fig. 13). Composites incorporating more as-cast wires than annealed wires (33 wires to 17 wires, respectively) exhibit distorted broad passbands and associated reflection and absorption peaks in the whole frequency range (Fig. 13(a)). In this case, the main contribution comes from the as-cast wires which deliver the passbands and the interface between the two regions which results in the splitting of the transmission spectrum. Meanwhile, the stopband structure exhibited for composites incorporating majority of annealed wires (17 as-cast wires to 33 annealed-wires, respectively, (Fig. 13(d)) demonstrate the dominant contribution of annealed wires to the EM signature. In particular, as in the case of composites containing only annealed wires B (Fig. 12(a)), dual stopbands are noticed in the A (17) + B(33) composites but with broader bandwidth (Fig. 13(d)). The single stopband displayed in composites incorporating only annealed wires C (Fig. 12(a)) also emerges in A(17) + C(33) composites, but with a much deeper dip. Hence, band features can be modulated by varying the vertical interfacial region in the composites.

The critical parameters that control the microwave response of the randomly dispersed wire composites include the intrinsic properties of the wires, wire concentration and the in-built interface between the two different regions. In the composites incorporating the same type of wires (Fig. 12(a)), the scattering is mainly influenced by the wire structure after the annealing process. As current annealing lowered the wire surface impedance, the scattering at the resonance increased and the rate of transmission was low (Makhnovskiy *et al.*, 2006). However, due to the closeness of crystallization and slightly larger magnetic anisotropy of the 40 mA-annealed wires (Uddin *et al.*, 2021) the surface impedance increased leading to higher transmission (Fig. 12(a)). For composites including the in-built vertical interface, not only the wire structure but the introduced vertical interface and wire concentration play a significant role in wave propagation. Electromagnetic waves are strongly localized near the interface of two different media and the amount of wave transmitted or reflected varies with the polarization state at the vertical interface. Through modulating the wire content in each region, the discrepancy between the permittivity or the ability to restrict and accumulate charges is varied, leading to distinctive interactions with EM waves. Fluctuations in wire loading also increase wave attenuation due to enlarged impedance contrasts (Genack and Garcia, 1993; Van Der Baan, 2001). A simple structure with merely 0.053 vol% of filler enables a highly tunable scattering spectra making the proposed plainification strategy instrumental for designing microwire metacomposites with broadband frequency selectivity without compromising lightweight feature or structural integrity.

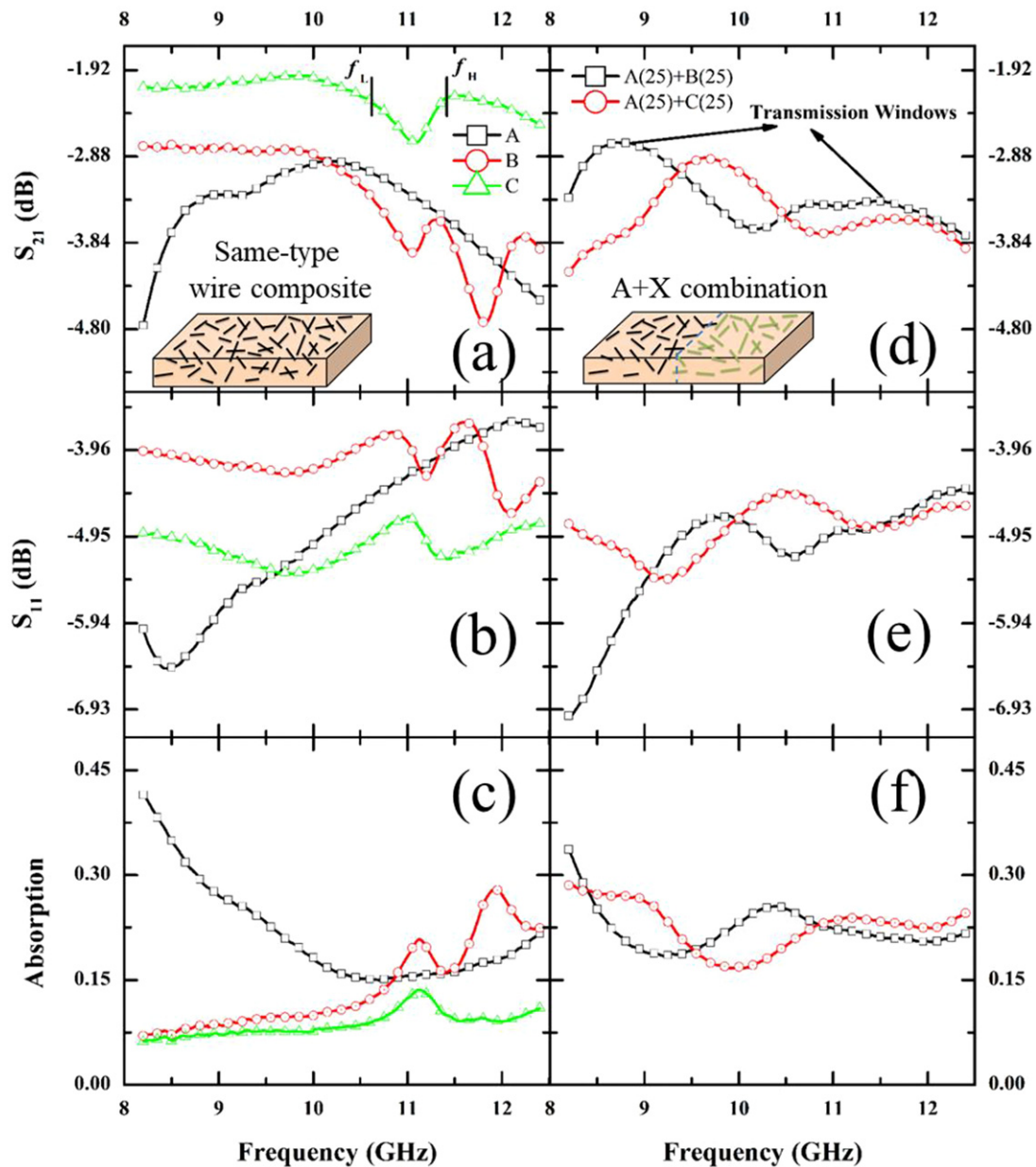


Fig. 12 Scattering properties: transmission S_{21} , reflection S_{11} , and absorption of the composites containing only one type of wires (left panel) and an equal combination of as-cast A and annealed X (right panel) randomly dispersed short-cut microwires. The labels f_L and f_H correspond to the two cut-off frequency points of the stopband feature. Reprinted from Uddin, A., Qin, F.X., Estevez, D., Peng, H.X., 2021. Vertical interface augmented tunability of scattering spectra in ferromagnetic microwire/silicone rubber metacomposites. EPJ Appl. Metamater. 8. Available at: <https://doi.org/10.1051/epjam/2021003A>. With permission from EDP Sciences.

Hybridization

Wire-wire hybrid metacomposites

Although the metacomposites containing orthogonal Fe-based wires ("Wire arrangement") expressed a natural DNG characteristic, its shift with respect to external field was minor. Fortunately, compared to Fe-based wires, Co-based microwires have a distinguished magnetoimpedance effect and thus their microwave response can be well modulated by external field/stress (García-Miquel *et al.*, 2010; Qin *et al.*, 2012a, 2010b). Thus, Co-based wires could be introduced to the existing Fe-based microwire metacomposites to realize tunable transmission windows by external stimuli. Moreover, the interplay between Co- and Fe-based wires in terms of alignment, intrinsic microwave properties and wire-wire dynamic interactions will be beneficial to expand DNG operating frequencies.

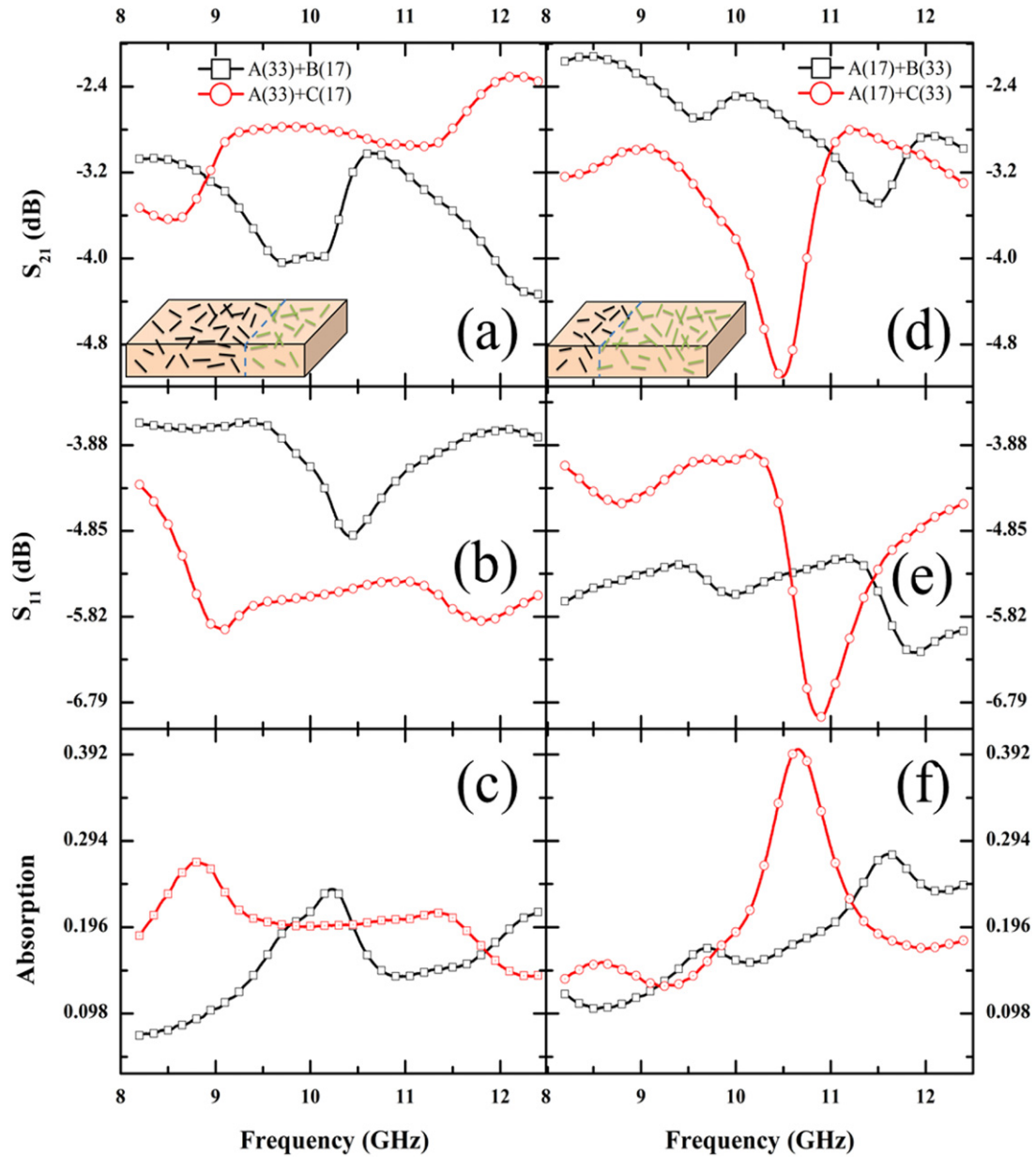


Fig. 13 Scattering properties: transmission S_{21} , reflection S_{11} and absorption of the composites containing different combinations of as-cast A and annealed X (30 mA, B or 40 mA, C) randomly dispersed short-cut microwires in separate regions and different proportions, i.e., 33 pieces of as-cast and 17 pieces of annealed wires (right panel) and 17 as-cast and 33 annealed wires (left panel). Reprinted from Uddin, A., Qin, F.X., Estevez, D., Peng, H.X., 2021. Vertical interface augmented tunability of scattering spectra in ferromagnetic microwire/silicone rubber metacomposites. EPJ Appl. Metamater. 8. Available at: <https://doi.org/10.1051/epjam/2021003A>. With permission from EDP Sciences.

Metacomposites incorporating a combination of continuous orthogonal Fe-based wire array and short-cut Co-based wires were prepared (Fig. 14) (Luo *et al.*, 2016). To avoid undesirable reflection loss from physical contact, Fe-based and Co-based microwires were hybridized in separate prepreg layers. Also to prevent microwave noise, a slight mismatch of approximately 1 mm between Co-based wire array Fe-based wires was intentionally introduced.

Fig. 15 displays the transmission and absorption of metacomposites containing respectively, single orthogonal Fe-based wires, short-cut Co-based wires, and their hybridized wire arrays. Composites incorporating short-cut Co-based wires reveal a typical band-stop feature described by a sharp transmission dip and absorption peak at 6 GHz. As previously mentioned, short wires behave as dielectric dipoles when interacting with the electric field of the incident wave. Taking ϵ_m as 3 (Ipatov *et al.*, 2009) and l as 15 mm into Eq. (9), we obtain $f_{\text{dres}} = 5.8$ GHz, which coincides well with the identified resonance peak in Fig. 15(b). The band-stop feature is maintained in the hybrid metacomposite and larger transmittance is achieved in the 1–6 GHz range compared to orthogonal Fe-based metacomposite. Hence, the introduction of short-cut Co-based wires facilitates the DNG feature in the

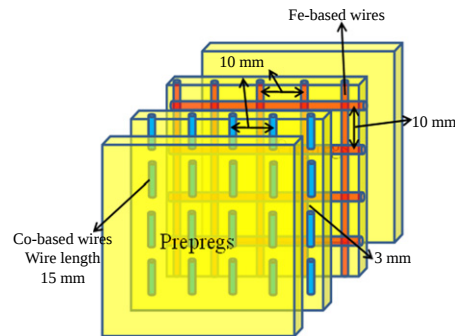


Fig. 14 Schematic illustration of the hybridization process of an orthogonal Fe-based microwire array plus a short-cut Co-based microwire array. Reprinted from Luo, Y., Qin, F.X., Scarpa, F., *et al.*, 2016. Microwires enabled metacomposites towards microwave applications. *J. Magn. Magn. Mater.* 416, 299–308. Available at: <https://doi.org/10.1016/j.jmmm.2016.04.089>. Copyright (2016), with permission from Elsevier.

metacomposites due to their low absorption loss (Fig. 15(b)). The short-cut wires generate a structure-associated opaqueness which results in a transmission enhancement at DNG operating frequencies. Therefore, the metacomposites could be engineered through manipulating Co-based wire spacing and arrangement to achieve specific transmission. This concept offers a potential application of the proposed metacomposites in the area of radio frequency identification (RFID). The RFID is a contactless data-capturing technique using RF waves to automatically identify objects that has found applications in commercial inventory, supermarkets, hospitals as well as friend-and-foe identification. By embedding these wire composites into the object to be detected which normally is a polymer-based material, a distinctive ID will be coded. Such configuration is advantageous compared to conventional RFID tags which are heavily disrupted by parasite coupling effects making the precise analysis of their EM signature rather difficult (McVay *et al.*, 2006; Jalaly and Robertson, 2005).

Up to now, we can clearly grasp the multiple merits of microwire metacomposites. Firstly, they are intrinsically different from conventional metamaterials where only the structure is usually exploited. Microwire metacomposites enable the design of DNG characteristics through both the material- and structural-associated parameters. Careful selection of the wire in terms of topological parameters and composition, and its structural modulation through e.g., current annealing determine DNG features at the mesostructural level. From the perspective of manufacturing, microwire metacomposites have a simplified arrangement and can be manufactured through a conventional polymer curing procedure. This is obviously more cost-effective and easier to achieve than top-down metamaterial fabrication techniques such as nanoimprint lithography (Chen, 2015; Gao *et al.*, 2014) and solid state superionic stamping (Chen *et al.*, 2019) or bottom-up techniques like self-assembly (Vignolini *et al.*, 2012).

Carbon fiber-wire hybrid metacomposites

We have concluded that arrays of ferromagnetic microwires are proper building blocks in metacomposites due to their tunable ferromagnetic resonance and tailorable geometrical characteristics. But what if we integrate such microwires into another functional fiber-reinforced polymer composite? Carbon fiber reinforced polymer (CFRP) composites are widely used in aerospace and automobile industries due to their light weight, high structural strength, and excellent anti-corrosion properties (Sandhanshiv and Patel, 2020; Yao *et al.*, 2018). Embedding microwire building blocks into CFRP composites could confer them with SNG or DNG properties and hence expand their applications to e.g., zero-loss structural health monitoring, microwave cloaking, and perfect absorbing. However, to effectively design such metacomposites, the concentration of carbon fibers should be carefully controlled considering their reflective nature which hinders the extraction of useful EM parameters. Additionally, the orientation of carbon fibers needs to be examined which results in highly anisotropic metamaterial features. These issues were evaluated when manufacturing CFRP metacomposites containing continuous and short-cut Fe-based microwires (Fig. 16) (Luo *et al.*, 2019).

Figs. 17 and 18 show the transmission coefficients of metacomposites containing microwires hybridized with short-cut and continuous carbon fibers, respectively. From Fig. 17, transmission windows are observed with a bandwidth of 1–6 GHz, which coincides with the result of the 3 mm parallel metacomposite (Fig. 4). This confirms that the DNG characteristic originates from the magnetic response of microwires and their periodic alignment. The transmission magnitude is also enhanced after the insertion of carbon fibers, increasing from -5.6 dB (circa 52.5%) (Luo *et al.*, 2013) to -1.6 dB (circa 83.2%) at zero field. The transverse conductivity between carbon fibers in the unidirectional CFPR composites is rather poor due to the electrically unconnected fibers (Athanasopoulos and Kostopoulos, 2011). As a consequence of E_k being placed perpendicular to the CFs, the permittivity of the wire-composites decreases and hence the impedance increases with the insertion of CFs. Therefore, the transmittance of a metacomposite containing CFs is improved accordingly. The reduced permittivity is verified by the imaginary part of the permittivity of which magnitude varies below 1.8 (inset of Fig. 17), suggesting a very weak dielectric response.

With respect to incorporating continuous carbon fibers, a series of transmission windows emerge under different magnetic fields (Fig. 18(a)). Phase velocity reversing from negative to positive values and negative permittivity (Fig. 18(c) and inset of Fig. 18(a)) are also observed. Remarkably, the amplitude of the observed windows linearly increases with magnetic field, i.e., the waves passing through the microwire metacomposite can be quantitatively controlled by application of magnetic bias. Meanwhile, neither field-tunable nor DNG features are indicated when E_k is along the CFs (Fig. 18(b) and (d)). The transmittance of the composites is rather

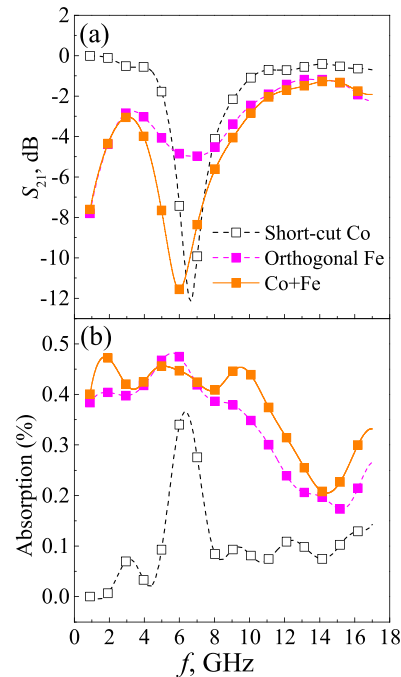


Fig. 15 (a) Transmission, S_{21} and (b) absorption coefficients of composites containing an orthogonal Fe-based wire array, a short-cut Co-based wire array, and their hybridized wire arrays in the absence of external fields. Reprinted from Luo, Y., Qin, F.X., Scarpa, F., *et al.*, 2016. Microwires enabled metacomposites towards microwave applications. *J. Magn. Magn. Mater.* 416, 299–308. Available at: <https://doi.org/10.1016/j.jmmm.2016.04.089>. Copyright (2016), with permission from Elsevier.

low with the lowest transmission obtained as -41.9 dB (0.8%), **Fig. 18(b)**. The transmission phase and permittivity results also suggest a double positive medium (**Fig. 18(d)** and inset of **Fig. 18(b)**). The anisotropic effect derived from the direction of electrical excitation field in the continuous CFs metacomposites resembles that of the orthogonal microwire metacomposites. However, the disappearance of the DNG properties in the former is due to the absence of microwires along the electrical excitation direction.

To summarize, two propagation modes were observed in the continuous CFRP metacomposite: highly transmitting mode with DNG feature and highly reflective mode with double positive index. Therefore, such composite component integrated with the anisotropic metamaterial function is capable of switching between cloaking and exposure by adapting its orientation to/against the electrical polarization without compromising the mechanical properties. The industry may benefit from such composites in e.g., modern friend-or-foe recognition, wherein CFRP composites are increasingly used.

Nanocarbon-wire hybrid metacomposites

Carbonaceous fillers have been increasingly used for modulating and optimizing the microwave properties of polymer-based composites due to their excellent conductive, thermal and mechanical performance (Qin and Brosseau, 2012). The distinctive dielectric response of composites including carbon structures such as carbon nanotubes (CNTs) and GO has recently led to the development of high-performance metamaterials (Yin *et al.*, 2018a,b; Wu *et al.*, 2018). The results indicate that the EM properties in these composites can be controlled through the size of the conductive carbon network. In the context of microwire composites, incorporating nanocarbons is promising to achieve controllable double/single negative characteristic and to build up a multi-scale composite towards practical applications. The hybridization of nanocarbon and Co-based microwires was achieved via electrophoretic deposition (**Fig. 19**) (Estevez *et al.*, 2018, 2019). The applied electric field and deposition time were crucial to control the deposition yield and thickness of the nanocarbon coating. Initially, the nanotubes forests are isolated in islands of various sizes and the coating is non uniform. Increasing the deposition voltage gives a more uniform CNT layer and nanotube networks can be easily formed. For the GO coated wires, the coatings treated at different annealing temperatures have the same basic morphology with distinctive graphene flakes dispersed on the wire surface. However, with increasing annealing temperature, the flakes appear thicker, which can be attributed to the restacking issue and thermally induced aggregation. By increasing the CNT content through variations in coating thickness, the size of the conductive CNT network and thus the permittivity can be efficiently controlled, as will be elucidated later. Meanwhile, regulating the number of oxygen-functional groups in GO through thermal reduction would lead to distinct carbon configurations and hence electromagnetic response. The nanocarbon/amorphous wire hybrid fibers were then incorporated in a parallel manner (3 mm fiber spacing) into silicone matrix and the EM parameters were measured in a WR-90 waveguide (**Fig. 19**).

Fig. 20(a) shows the permittivity as function of frequency of composites containing CNT-coated wires with different coating thicknesses (Estevez *et al.*, 2019). Clearly, the thickness determines the dielectric properties and is therefore a route to tune the negative permittivity. With increasing the coating thickness a transition from Lorentz resonance to Drude plasma oscillation for the

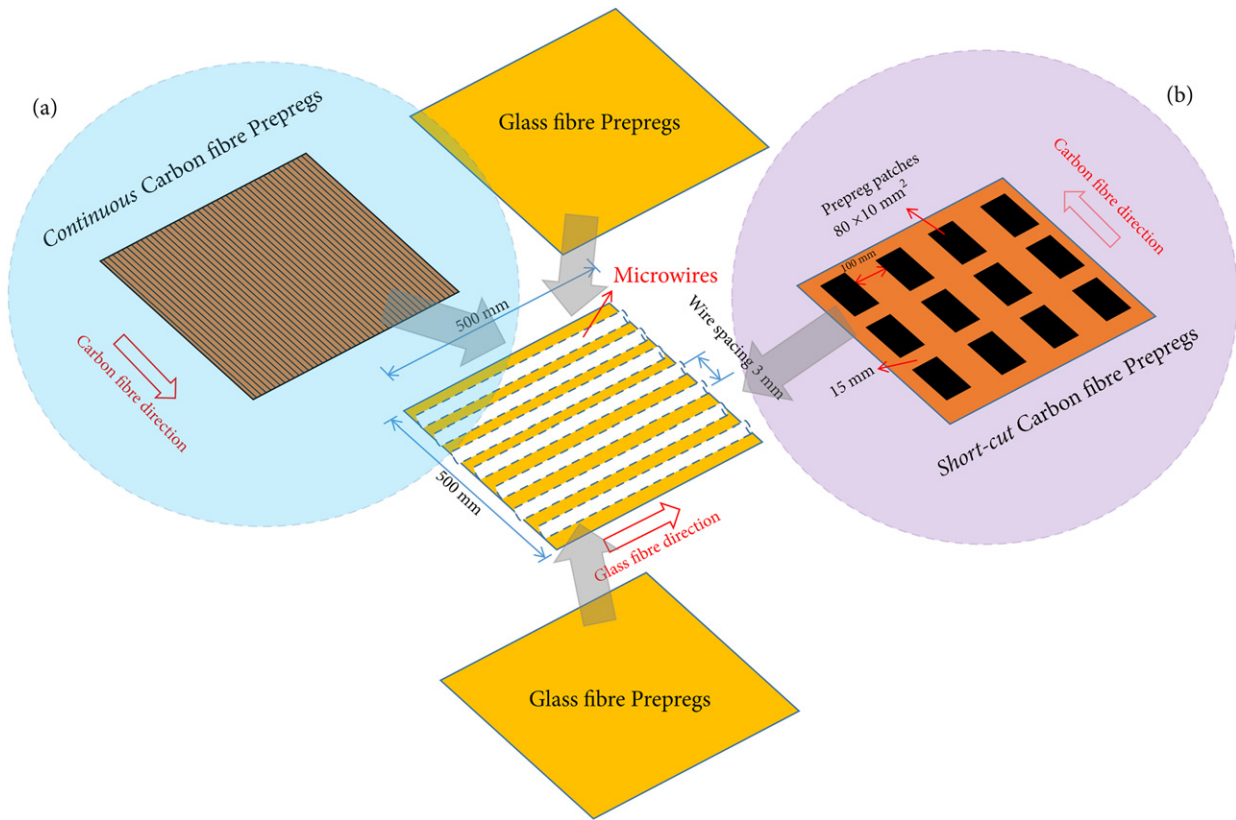


Fig. 16 Schematic diagram of metacomposites containing 3 mm spaced parallel Fe-based microwires and (a) continuous and (b) short-cut carbon fibers. Reprinted from Luo, Y., Estevez, D., Scarpa, F., *et al.*, 2019. Microwave properties of metacomposites containing carbon fibres and ferromagnetic microwires. Research 2019, 1–8. Available at: <https://doi.org/10.34133/2019/3239879>. With permission from AAAS.

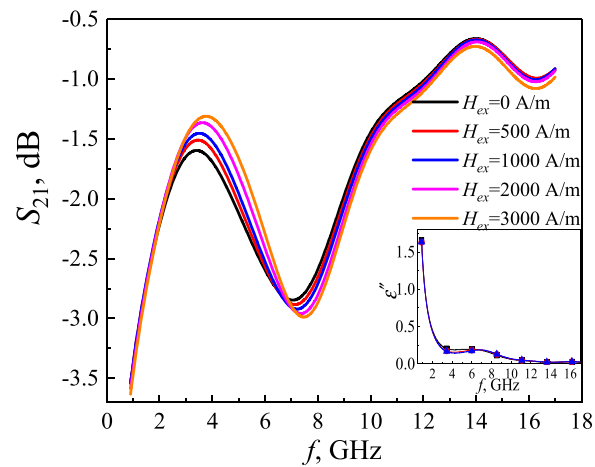


Fig. 17 Frequency dependence of transmission S_{21} coefficients of the short-cut CFRP metacomposites in the frequency range of 0.7–17 GHz under an external magnetic bias up to 3000 A/m. The inset is the imaginary part of the permittivity of the same metacomposite. Reprinted from Luo, Y., Estevez, D., Scarpa, F., *et al.*, 2019. Microwave properties of metacomposites containing carbon fibres and ferromagnetic microwires. Research 2019, 1–8. Available at: <https://doi.org/10.34133/2019/3239879>. With permission from AAAS.

frequency dispersion is observed. Such conversion can be explained based on the inter-connectivity of the CNT on the wire surface (Fig. 20(a)): (1) for the wire coated with 1.73 μm CNTs, owing to the non-uniformity of the CNT coating, electrons have a hopping-like behavior (Cheng *et al.*, 2017) resulting from the induced electric dipole in isolated CNTs and therefore overshadows the plasmonic behavior; (2) further increasing the coating thickness leads to the inter-connectivity of the CNTs, rendering electrons delocalized and free to move throughout the system. In this case, plasma oscillation can describe the dielectric behavior since the

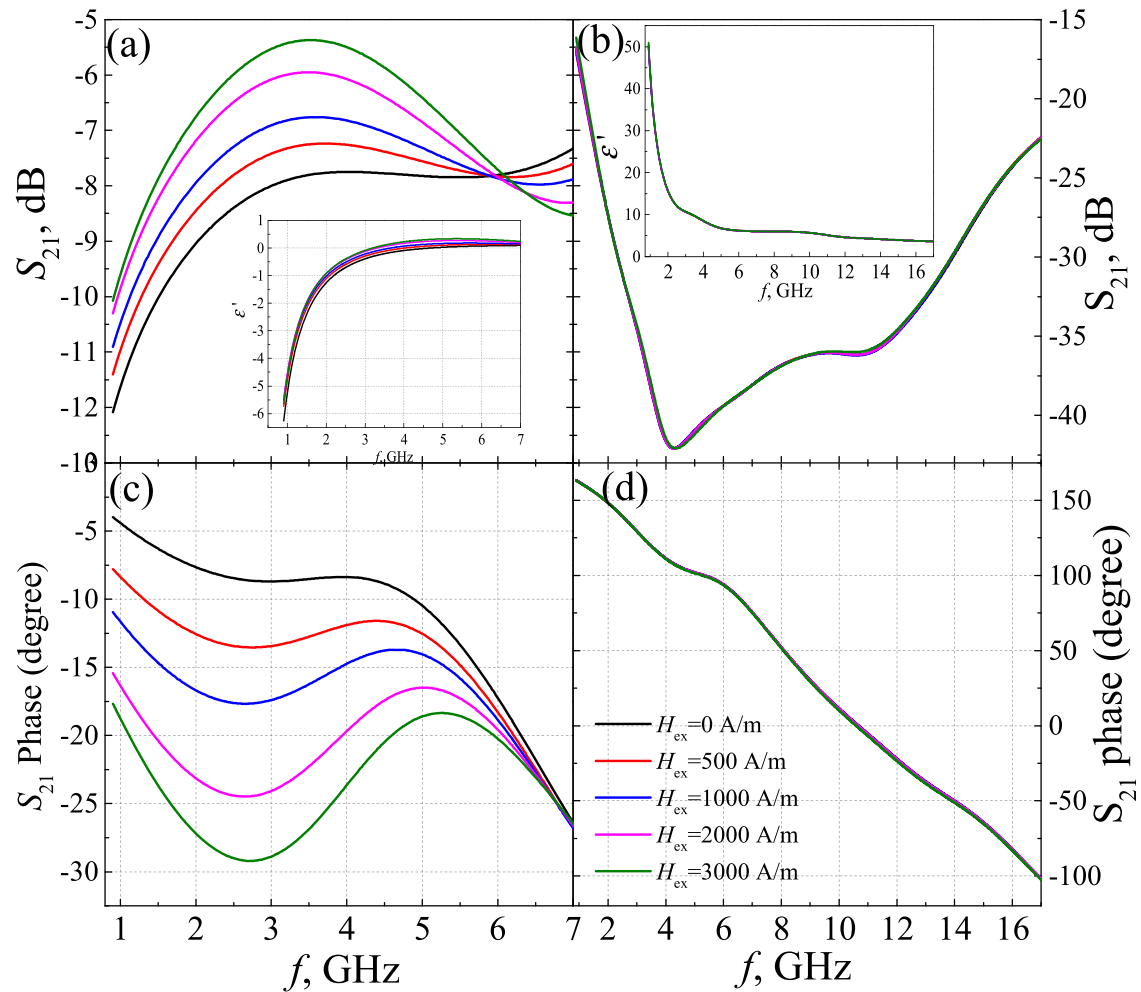


Fig. 18 Frequency plots of transmission spectra of hybrid metacomposites containing continuous carbon fibers with E_k placed (a) along and (b) perpendicularly to the microwires. Frequency plots of transmission phase of the same composite in (a)/(b) with E_k (c) along and (d) perpendicular to the microwires. The insets in (a) and (b) are the frequency dependences of their ϵ' when E_k is along and perpendicular to the microwires, respectively. Reprinted from Luo, Y., Estevez, D., Scarpa, F., *et al.*, 2019. Microwave properties of metacomposites containing carbon fibres and ferromagnetic microwires. Research 2019, 1–8. Available at: <https://doi.org/10.34133/2019/3239879>. With permission from AAAS.

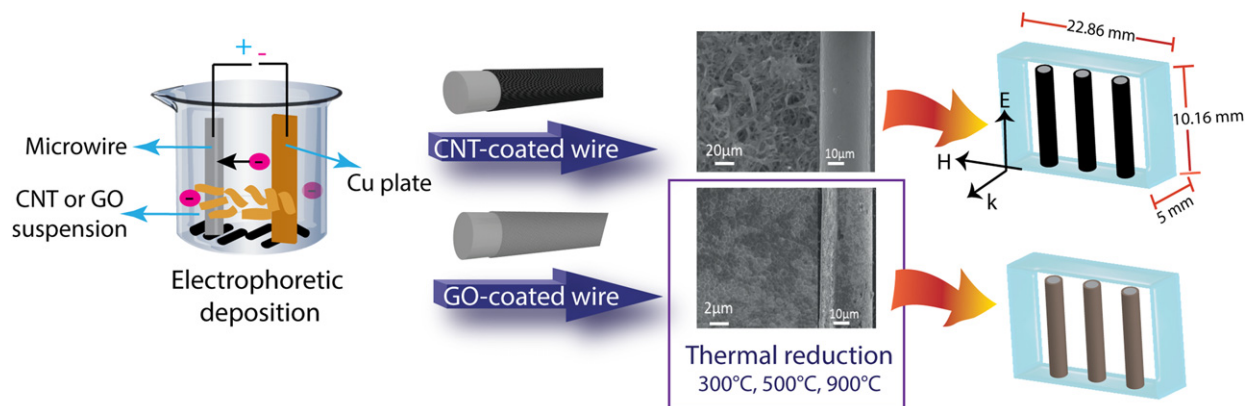


Fig. 19 Preparation of nanocarbon-coated microwires by electrophoretic deposition, morphology of the CNT and GO coatings and incorporation of the hybrid fibers into polymer matrix for EM testing. Modified from Estevez, D., Qin, F., Luo, Y., *et al.*, 2019. Tunable negative permittivity in nano-carbon coated magnetic microwire polymer metacomposites. Compos. Sci. Technol. 171, 206–217. Available at: <https://doi.org/10.1016/j.compscitech.2018.12.016>. Copyright (2019) with permission from Elsevier.

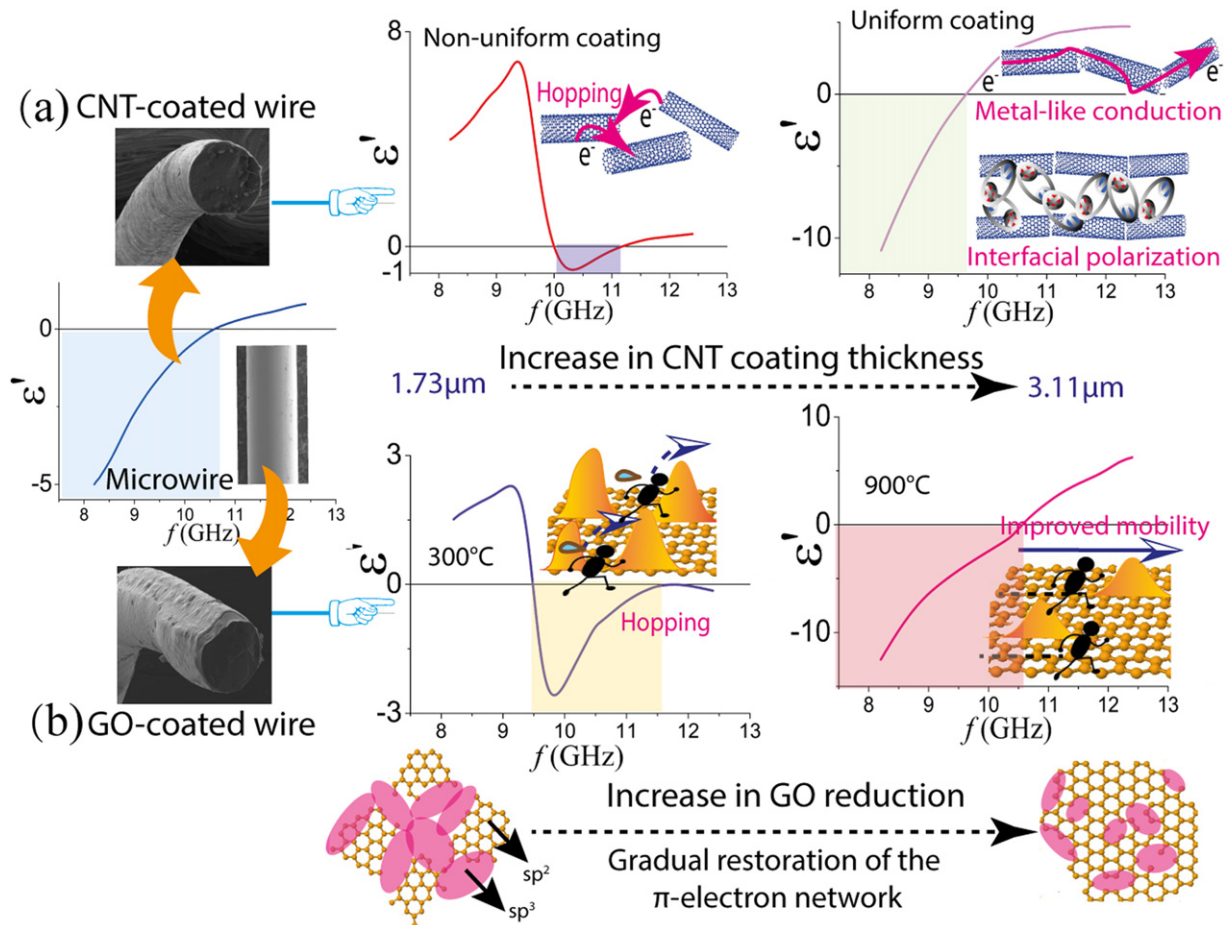


Fig. 20 Frequency permittivity spectra of (a) metacomposites incorporating CNT-coated wires with different CNT coating thickness and (b) metacomposites incorporating GO-coated wires with different GO reduction temperatures. The inset schematics show the corresponding mechanism involved in the conversion from Lorentz-like negative permittivity to Drude-like permittivity. Adapted from Estevez, D., Qin, F., Luo, Y., *et al.*, 2019. Tunable negative permittivity in nano-carbon coated magnetic microwire polymer metacomposites. *Compos. Sci. Technol.* 171, 206–217. Available at: <https://doi.org/10.1016/j.compscitech.2018.12.016>. Copyright (2019) with permission from Elsevier.

hybrid wires can be regarded as metal-like elements in the metacomposites. In addition, with increasing thickness, the coating also tends to become layer-wise, and hence the interfacial polarization between the layers is enhanced further influencing the negative permittivity (Estevez *et al.*, 2019).

Interestingly, the conversion in the frequency dispersion of permittivity is also observed in the metacomposites containing GO-coated wires with increasing thermal reduction degree (Fig. 20(b)) (Estevez *et al.*, 2019). Firstly, it was demonstrated that GO-coated wires without any thermal reduction realize positive permittivity due to the large amount of oxygen functional groups, which are non-conductive and yield a trivial response to the electric field (Estevez *et al.*, 2019). Remarkably, when the hybrid fibers are annealed at 300°C, the permittivity curve resembles that of the CNT-1.73 μm coated amorphous wire (Fig. 20(b)) described by the Lorentz model. Further thermal reduction of GO-coated wires at 900°C leads to switching from resonance-like to plasma-like behavior with negative permittivity values below the plasma frequency fitted by the Drude model. To understand this transition, one should scrutinize the structural transformation during the reduction of GO. Oxygen-containing functional groups in GO contain variable sp^2 and sp^3 domains, and therefore, the resultant electrical properties are dictated by the size, shape, and relative fraction of such domains (Wang *et al.*, 2017). At a low reduction temperature, restoration of the graphitic structure is insufficient, resulting in an electrical structure of small sp^2 clusters or domains surrounded by large sp^3 domains (Wang *et al.*, 2017) (Fig. 20(b)). Due to electron confinement such isolated sp^2 domains have a large energy gap, hence increasing the barrier height and leading to the formation of electron-hole puddles (Bhaumik and Narayan, 2016). As a result, the carrier transport properties in composites containing GO-coated wires annealed at 300°C can be depicted by a hopping model via the localized states in the large energy gap (Fig. 20(b)) leading to a Lorentz-type dielectric resonance. Further thermal reduction of the hybrid fibers creates new and large sp^2 clusters caused by the gradual restoration of the graphitic structure through the removal of oxygen which provides pathways between sp^2 domains already present (Wang *et al.*, 2017; Bhaumik and Narayan, 2016). The expansion of the delocalized π -electron leads to a decreased potential barrier among domains, and continuous conduction with a small energy gap becomes possible (Fig. 20(b)). Thus, a Drude plasma-like negative permittivity behavior emerges in the metacomposites containing rGO-coated wires annealed at 900°C.

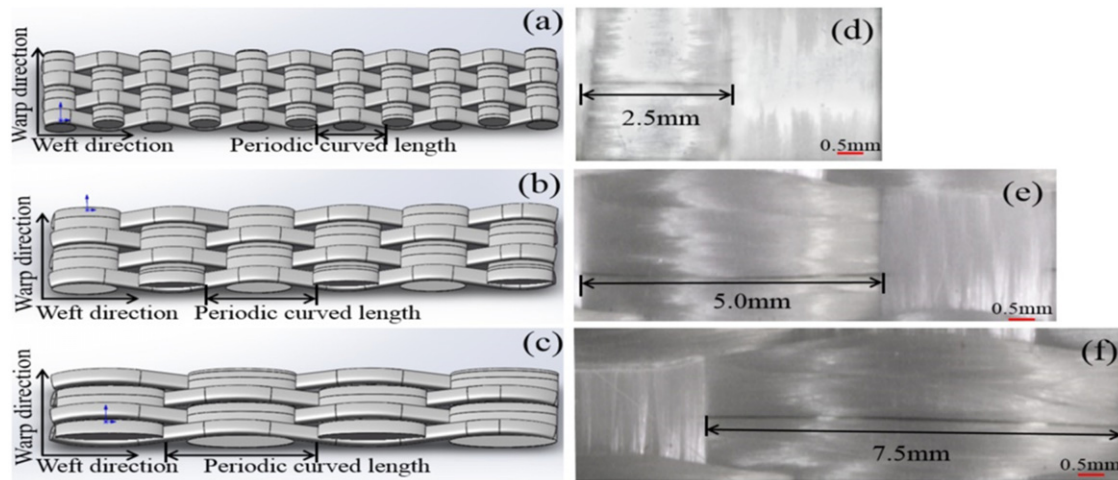


Fig. 21 Schematic representation of the interwoven microwires with periodic curved length of (d) $S_1 = 2.5$ mm, (e) $S_2 = 5$ mm and (f) $S_3 = 7.5$ mm. Reprinted from Jiang, Q., Xiang, C., Luo, Y., *et al.*, 2020a. Design and X-Band electromagnetic response of single negative metacomposite containing periodic curved Co-based ferromagnetic microwires. *J. Mater. Res. Technol.* 9, 4593–4603. Available at: <https://doi.org/10.1016/j.jmrt.2020.02.087>. Copyright (2020), with permission from Elsevier.

Overall, hybridizing microwires with nanocarbon coatings to assemble metacomposites provides basic design guidelines for realizing single-negative dielectric properties. A homogeneous coating of CNTs and high GO reduction are preferred for comparable operating frequencies and if higher values of negative permittivity are expected. Other determining factors include interfacial polarization, defects and surface roughness (Estevez *et al.*, 2019). By coating the amorphous wire with nanocarbons, the negative dielectric features can now be tunable to a great extent, making this strategy more effective than applying a magnetic field or adjusting the wire arrangement.

Textile reinforcement

Textile structure has distinctive advantages in tuning EM behavior of composites due to its high structural flexibility. By adjusting textile structure from 3D interlocking woven to orthogonal structure, different absorption responses were realized (Fan *et al.*, 2018a,b). For instance, Wang *et al.* fabricated a microwave sandwich composite incorporating a graphene-based fabric between glass fiber and carbon fiber clothes (Wang *et al.*, 2018). Therefore, weaving technique is a feasible option to integrate both metamaterial units and reinforcement simultaneously. Based on this research, the idea of building metacomposites by incorporating continuous microwires in weave structure emerges. In this structure, the interweaved microwire arrays constitute metamaterials units while at the same time serve as reinforcement. Jiang *et al.* (2020a,b) proposed to use Co-based microwires as periodical units interweaved into textile preform to realize metacomposites (Fig. 21). The complex permittivity and permeability were manipulated by tailoring the wire alignment, curved length and wire spacing. The microwires were incorporated into the quartz fabric at periodic lengths of $S_1 = 2.5$ mm; $S_2 = 5$ mm and $S_3 = 7.5$ mm and resin transfer molding (RTM) was adopted in the composite preparation. To investigate the effect of alignment on EM performance, the samples were cut along the horizontal (S_H) and vertical directions (S_V) for EM test.

From Fig. 22, the curvature and arrangement of the microwires clearly affect the electromagnetic response and microwave propagation of the metacomposites. Only composites containing vertically-arranged microwires (Fig. 22(b)) exhibited Lorentz-like negative permittivity due to the dielectric resonance of microwire arrays while their real part of permeability was higher than that of horizontally-arranged microwires. On the other hand, the introduction of periodic curved microwires exerted trivial influence on the mechanical properties but was pivotal on homogenizing the strain and reducing the stress concentration in the metacomposites. Apart from the amenable microwave single negative properties, these metacomposites are featured with excellent structural properties which could expand further their applications in e.g., structural health monitoring, sensing and stealth applications.

External Stimuli

Stress

Due to the significant stress impedance effect of ferromagnetic microwires, the application of stress exerts a significant impact on the wave propagation mode in microwire metacomposites. For stress-sensitive microwire composites, a substantial deviation of the wire magnetic anisotropy from the circumferential direction (ideal case: axial anisotropy) would be preferred (Makhnovskiy *et al.*, 2006). As demonstrated in previous sections, for composites containing microwires with large magnetoimpedance effect at microwave frequencies, the effective permittivity may depend on magnetic field via the corresponding dependence of the surface impedance. Additionally, the surface impedance can be modified by applying stress which alters the wire magnetic anisotropy and domain structure and thus the permittivity. Consequently, the stress impedance property of microwires is critical to the stress sensitivity of the whole composite conditioned by wire composition, geometry and domain structure. This accounts for the variable stress dependence of

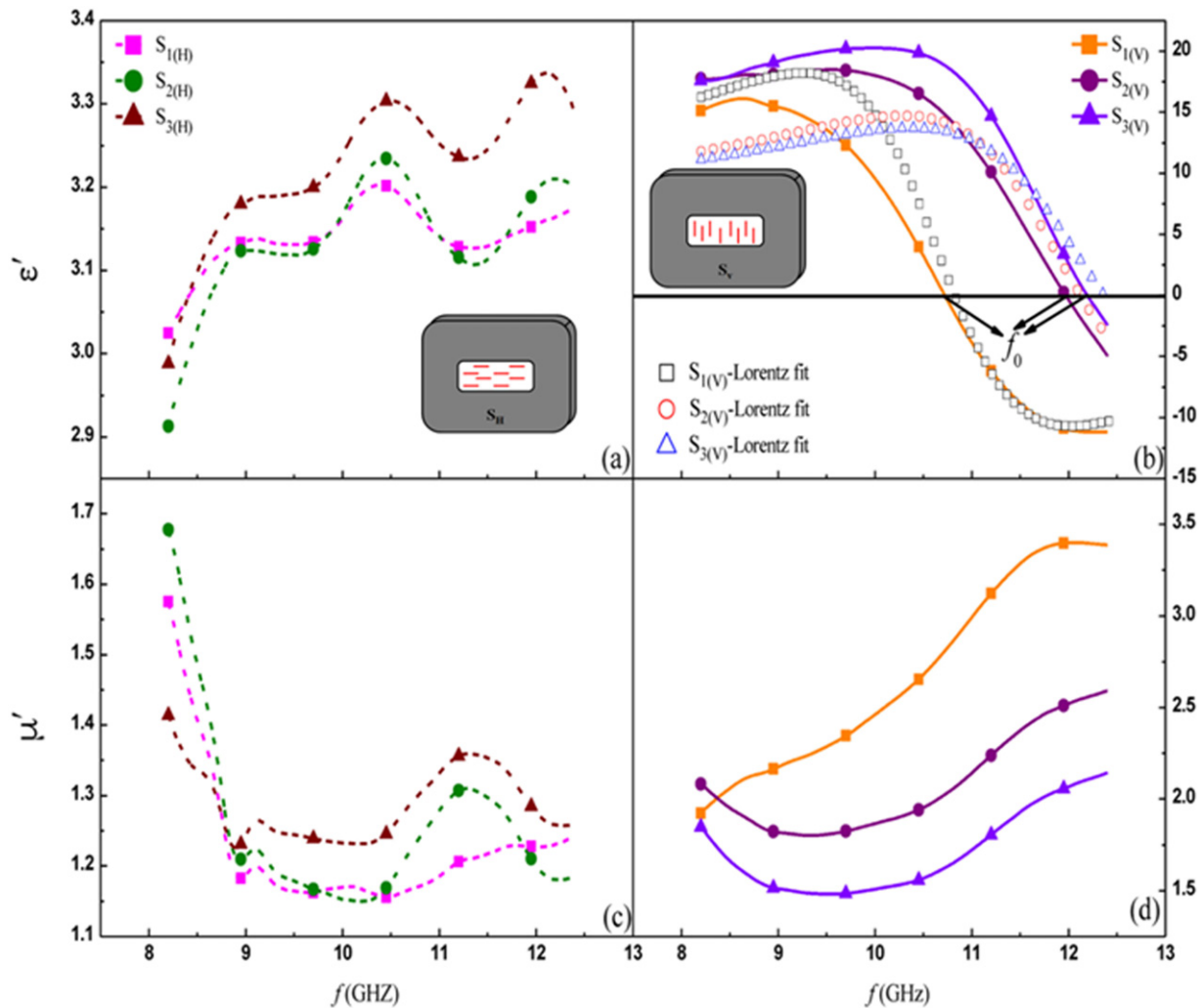


Fig. 22 Real part of permittivity (ϵ') and permeability (μ') of metacomposites with periodic microwires at a curved length of $S_1 = 2.5$ mm, $S_2 = 5$ mm and $S_3 = 7.5$ mm and horizontally (a/c) and vertically-arranged (b/d). The inset figures represent the different alignments of microwire arrays for EM testing. Reprinted from Jiang, Q., Xiang, C., Luo, Y., *et al.*, 2020a. Design and X-Band electromagnetic response of single negative metacomposite containing periodic curved Co-based ferromagnetic microwires. *J. Mater. Res. Technol.* 9, 4593–4603. Available at: <https://doi.org/10.1016/j.jmrt.2020.02.087>. Copyright (2020), with permission from Elsevier.

permittivity in microwire composites incorporating different types of wires (Qin *et al.*, 2012b). In the case of Co-based microwires with negative magnetostriction, the application of stress along the wire axis induces a magnetoelastic field in the circumferential direction rotating the spins towards that direction (Peng *et al.*, 2016). As a result, the circumferential permeability is decreased lowering the surface impedance. Therefore, the application of a longitudinal stress will compensate the effect of magnetic field (Qin *et al.*, 2011).

Apart from optimizing composition and magnetic structure of the wire fillers, another way to improve stress sensitivity is by increasing the amount of microwires in the composites. However, it does not necessarily mean that the more the better. In Co-based microwire composites, increasing the wire number from 6 to 17 the sensitivity of permittivity to stress showed little change (Qin and Peng, 2013). This observation suggests that the stress sensitivity in Co-based wire composites is independent of wire conductivity and permeability for a sufficiently high concentration of wires (Qin *et al.*, 2012b). Therefore, in a large context, the macroscopic behavior of microwire composites depends on the collective response of the wires on the one hand, and on the individual response of each wire on the other hand.

Magnetic field

In previous sections, we have already discussed partially the effect of magnetic field on tuning the double negative properties of microwire composites. The negative permeability could be adjusted by taking into account the ferromagnetic resonance of the wires. The permeability parameter is rather insensitive to moderate magnetic fields since at such frequencies the condition of the ferromagnetic resonance requires a much stronger magnetic field. Meanwhile, for the wire radius at the micron scale, and wire spacing in mm scale, the plasma frequency which determines the negativity permittivity falls in the GHz range. In this frequency band, the permittivity dispersion may be used to engineer a specific tuneable electric response by tuning the losses with an external magnetic field or stress which

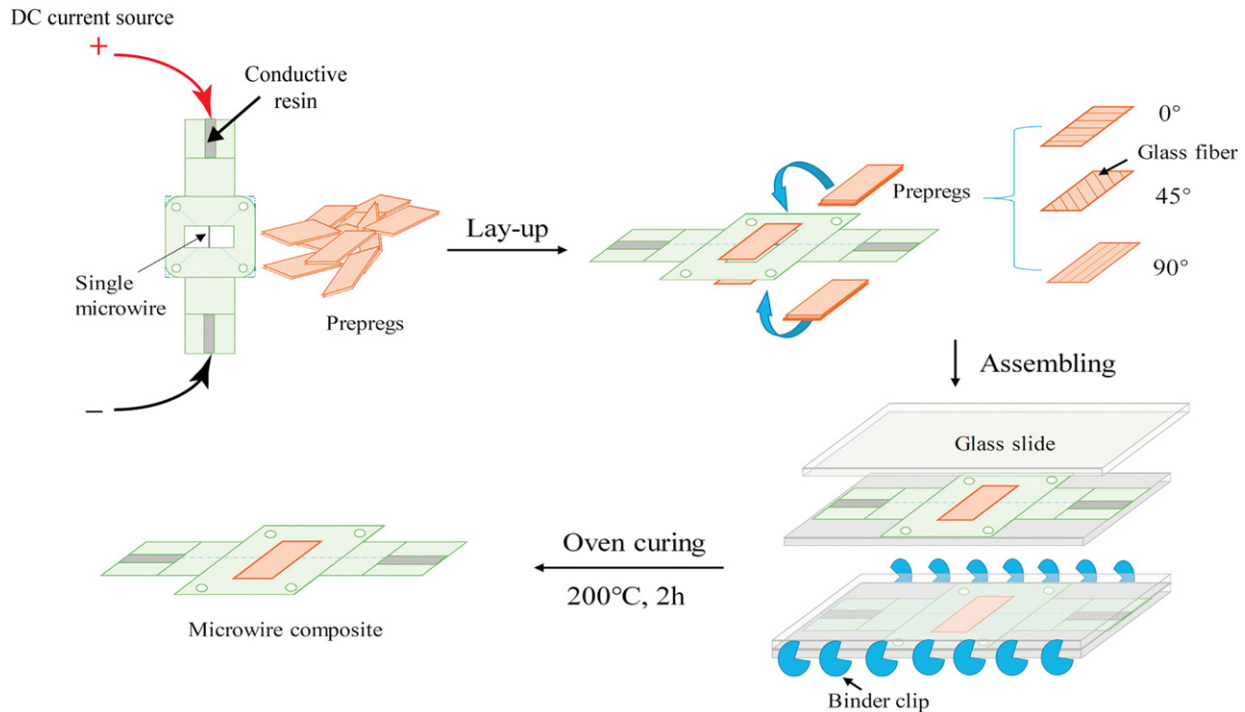


Fig. 23 Manufacturing process of in-situ electric field responsive microwire metacomposites. The wires were sandwiched between two prepregs at 0°, 45° and 90° with respect to the glass fiber direction. Modified from Zhao, S., Qin, F., Luo, Y., *et al.*, 2020a. Responsive left-handed behaviour of ferromagnetic microwire composites by in-situ electric and magnetic fields. *Compos. Commun.* 19, 246–252. Available at: <https://doi.org/10.1016/j.coco.2020.04.012>. Copyright (2020) with permission from Elsevier.

produces a change in the wire magnetic configuration (Panina *et al.*, 2011b). The extent of the field-tuning depends not only on magnetoimpedance effect but also on the geometrical parameters of the wires and their spacing, which has been extensively confirmed previously (Luo *et al.*, 2013, 2014b). Thus, it is viable to modulate or optimize the microwave dielectric properties and transmission/reflection patterns of metacomposites through tuning wire parameters, which can also be implemented to extend the effective operation frequency range of DNG features. When it comes to the design and manufacture of microwire metacomposites for field tunable functionality, careful choice of wires proves to be critical to the ultimate performance of the composites.

Current

To further demonstrate the tunable left-handed capabilities towards external stimulus of microwire composites, S. Zhao *et al.* proposed to apply an in-situ DC current to manipulate the transmission spectra (Zhao *et al.*, 2020a,b). A wire of 120 mm in length was placed on a supporting sheet having a rectangular opening matching the size of the waveguide cavity (Fig. 23). The glass coating was removed from the wire ends to ensure a good electrical conductivity. A second sheet was fixed on the top to ensure non-contact between the wire and the waveguide fixture. Additionally, part of the supporting sheet contained conductive resin and was left outside the waveguide to allow connection to the DC current source. The wire was then sandwiched between two prepregs at 0°/45°/90° relative to the glass fiber direction followed by the addition of two more prepreg layers on top and bottom, respectively (Fig. 23). The specimens were cured at 200°C for 120 mins followed by a natural cooling process.

Remarkably, the transmission window of the free-standing wire becomes more prominent when incorporated into the prepregs (Fig. 24 (a)), which is closely related to the introduced interface when the microwire is placed along the reinforcing fibers. When the DC current is increased to 100 mA (Fig. 24(b)), two marked transmission windows emerge. These transmission windows shift to lower frequency with increasing angle of microwire alignment. In this case, stresses are homogeneously transferred from the matrix to the metallic core during the curing process, enhancing the wire circumferential domains. For 0° alignment (Fig. 24 (c, d)), large compressive stresses are exerted on the microwire due to the different thermal expansion coefficients between the microwire and polymer matrix. As a result, the anisotropy field of the microwire is modified (Adenot *et al.*, 2004) which is reflected in the shifting of transmission spectra to lower frequency. For a 90° alignment, surface stresses on the microwire change from radial compression to circumferential shear force, leading to a smaller anisotropy field and thus higher sensitivity to DC current. Therefore, by simultaneously exploiting the response to external stimuli and the metacomposite manufacturing parameters, frequency-selective wave transmitting structures for potential sensing and cloaking applications could be developed.

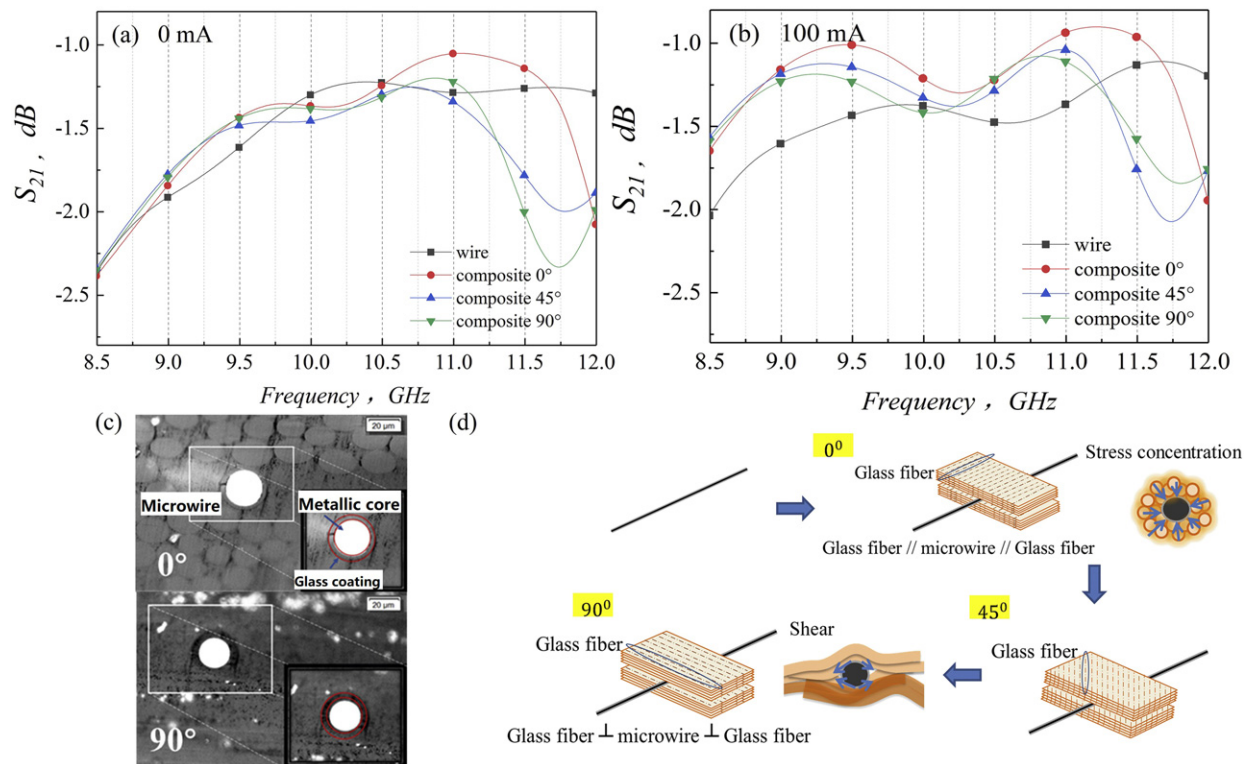


Fig. 24 Frequency plots of the transmission coefficients, S_{21} , of Co-based microwire composites with an in-situ current of (a) 0 mA and (b) 100 mA in the presence of an external magnetic field of 8 Oe; (c) The cross section of composites containing Co-rich microwires aligned at 0°/90° degrees with respect to the glass fibers; (d) Schematic view of the stress distribution of composites containing Co-rich microwires aligned at 0°/45°/90° degrees with respect to the glass fibers. Reprinted from Zhao, S., Qin, F., Luo, Y., *et al.*, 2020a. Responsive left-handed behaviour of ferromagnetic microwire composites by in-situ electric and magnetic fields. *Compos. Commun.* 19, 246–252. Available at: <https://doi.org/10.1016/j.coco.2020.04.012>. Copyright (2020) with permission from Elsevier.

Manufacturing and Application Prospects of Microwire Metacomposites

Manufacturing

Microwire metacomposites are defined as a category of engineering materials and thus optimizing their manufacturing process is essential. The manufacture of microwire metacomposites is primarily reduced to solve the automation of prepreg machining and the wire/prepreg placement and combination before the preform or curing process begin. The first step for metacomposite fabrication is cutting the prepregs according to specific design requirements. Currently, with the increase of composites production facilities and tighter part tolerances and specifications, manual cutting is no longer viable. Fully automated prepreg cutting machines are now used for cutting various types of prepreg. Automated cutting equipment can speed up production and reduce labor costs. The key features of prepreg cutting machines are optimal material usage by using nesting software to enable the cutting of different shapes/profiles of prepregs with required orientations. Fig. 25 shows an example of an automated prepreg cutting machine. Such machine enables to cut prepregs with great accuracy and edge quality without sacrificing speed. The laser pointer allows pointing precision of less than 0.76 mm at the vibration frequency of 200 Hz.

The next step in the manufacturing process is the lay-up of the prepregs and wires. While manual layup enables a high degree of detail in preform manufacturing, automatic processes have proven to be more economic and less prone to human error during the critical pre-mold steps. To load the prepreg with the microwires, we employ a unique winding system that pulls the prepreg around a series of evenly spaced pins at each end of the machine (Fig. 26). While the mandrel rotates at a pre-programmed speed rate, the winding head pulls the resin impregnated-wire back and forth around the pins in 0° orientation. A “pipe” shape is formed by all longitudinally-arranged wires. Successive layers are added at the same or different winding angles until reaching the required thickness. Using this setup enables the control of winding angles and the placement of the wire reinforcement (Fig. 26).

The last stage in the manufacture of microwire composites involves the autoclave curing. For this purpose, we use an aerospace-grade ASC autoclave (Fig. 27(a)) equipped with a curing chamber of 1.6 * 2 m², maximum working pressure of 7 bars and maximum working temperature of 250°C. The autoclave includes controls, part thermocouples, and part vacuum lines. Additionally, it also enables cooling of the part, thus decreasing production time and ensuring safe post-cure handling. Using this autoclave, microwire metacomposites with finer detail, tighter tolerance, lighter weight, increased strength, and lower porosity can be prepared (Fig. 27 (b)).



Fig. 25 Gerber digital DCS 2600 prepreg cutting machine.

Applications

Upon understanding the influence of metacomposite architecture such as wire intrinsic parameters, wire periodicity and composite manufacturing, we are ready to move on to discuss application perspectives. The presented results demonstrate solid possibilities of microwire metacomposites in developing cloaking devices due to the enhanced transmission spectra. As previously highlighted, the wire metacomposites could be also used in RFID. Composites containing microwire arrays offer a versatile solution and a simple structure that could be incorporated into the objects to be detected with each object having a unique ID coded in these composites. The use of microwire metacomposites could also enhance the radiated power of an antenna. Negative permittivity and permeability of these engineered structures can be utilized for making electrically small, highly directive, and reconfigurable antennas. These, metacomposite-based antennas may demonstrate improved efficiency and bandwidth performance. They can be promising candidates as antenna substrates for miniaturization, sensing, bandwidth enhancement and for controlling the radiation direction. Microwire metacomposites could be also suitably designed to use as radome. Radome is mainly used as a covering to protect an antenna from rain, wind perturbations, aerodynamic drag, and other disturbances with minimal impact on the antenna electrical performance. The use of microwire metacomposites as metamaterial “covers” could modulate characteristics such as transmission losses and bandwidth of the enclosed antenna and add new features, like band-pass or stimuli-responsive switchable features.

Aircraft components and the composites they are built from require being as light as possible while still able to carry out their role. These components often carry high loads, and their lightweight nature means that even small flaws can lead to failure. Testing for flaws is essential, but needs to be carried out in a non-destructive way. In general, failures occur when a component or structure is no longer able to withstand the stresses imposed on it during operation. Non-contact methods such as ultrasonic and acoustic testing, for example, allow us to detect existing defects only. They provide no indication of internal stresses in a material or stress distribution throughout the structure. Traditional methods for stress monitoring are contact-based, requiring physical tag attachment to the material. As aforementioned, microwire metacomposites constitute a system sensitive to applied stress. The tensile stresses in the matrix surrounding the microwires affect the microwire response to an incident electromagnetic field. Therefore, a contactless type sensor that measures variations of electromagnetic properties resulting from stress variations can be designed. The advantages of these microwire composites for structural health monitoring relies on their simple and cheap preparation method, insulation against harsh environment through the glass-coating of the wire and the possibility of miniaturization. Therefore, by employing microwire-embedded composites the process of stress monitoring could be much easier, faster and more efficient, allowing to detect the emergence of barely invisible damages in a wireless way (Zhao *et al.*, 2020a,b).

Summary and Outlook

Metamaterials have aroused wide interest in recent years enabling a number of fascinating emerging technologies. Nevertheless, the drawbacks of artificially constructed metamaterials are as significant as their merits, such as high manufacturing costs, complex internal structures, poor tunability and independence of the intrinsic properties of constituent structures. These issues are addressed by introducing a new concept, “metacomposite”, which is a composite material that takes its properties from both the composite fillers as functional units and their prescribed ordered structure at single or multiple length scales. It is defined by the following three aspects: (1) metacomposites are a true piece of material rather than a meta-structure, (2) the final properties are dependent on the properties of their constituents and mesoscopic parameters in terms of topological configuration, and (3) their metamaterial properties can be exploited following a simple engineering fabrication method.

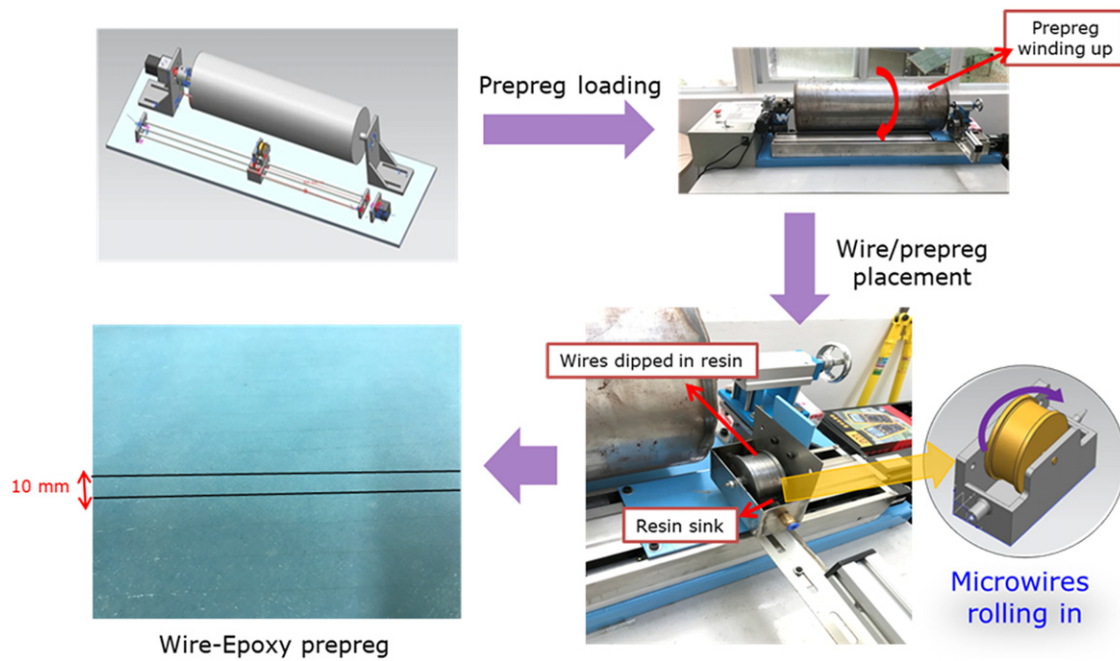


Fig. 26 An in-house built prepregs and microwire winding machine for the microwire-prepreg automation at InCSI.

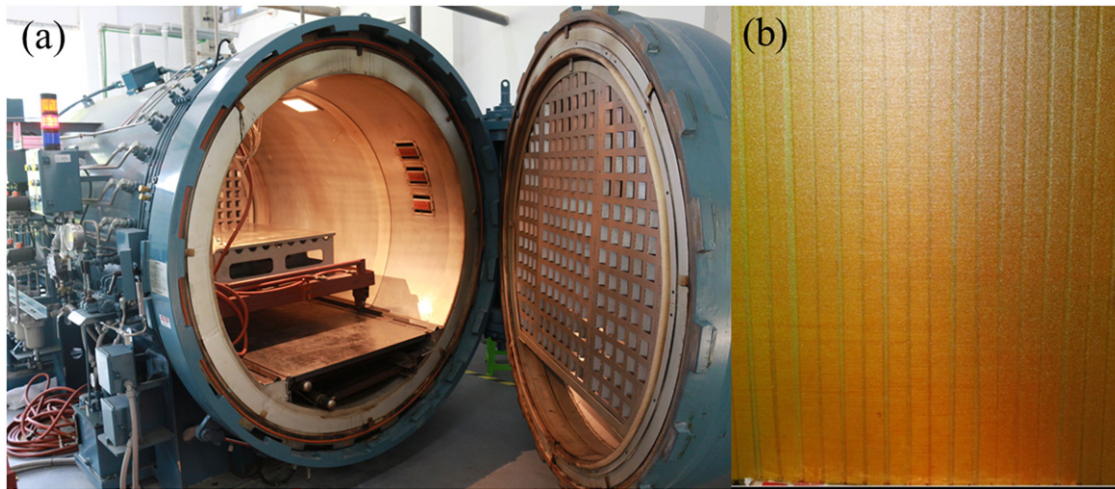


Fig. 27 (a) Aerospace-grade ASC autoclave for the composites curing (b) an example of microwire metacomposites, which contains parallelly arranged microwires in a glass-fibre reinforced polymer.

The metacomposite term was initially applied to composites containing nano-/micro-fillers, particularly through achieving a negative permittivity nanocomposite by coating polypyrrole on the surface of WO_3 nanoparticles. The idea was further extended to several other dielectric and magnetic fillers in 0D, 1D or 2D forms. Even though these metacomposites are inspiring, they are unlikely to be adopted for engineering purposes due to their narrow SNG or DNG bandwidth and delicate processing techniques. Enlightened by the excellent magnetic properties of ferromagnetic microwires and particularly their usefulness in enabling multifunctional polymer composites, we highlighted a novel type of metacomposites containing microwires and their optimization. The capability of microwires to realize metamaterial features was first presented employing the most basic metacomposite configuration, i.e., Fe-based microwires arranged in a parallel manner. In such metacomposites, a natural DNG characteristic was observed as evidenced by a transmission window and a negative permittivity dispersion in the 1–7 GHz range. Although DNG indices were obtained in such simple configuration, issues such as low transmission level, high reflection losses and narrow band of DNG feature remained. Further optimization was then presented based on microwire intrinsic properties, topological configuration and the incorporation of other functional fillers which enabled to modulate magnitude and frequency band of left-handed features. With respect to meso-micro structural parameters, Co-based microwires present larger effective permittivity and enhanced

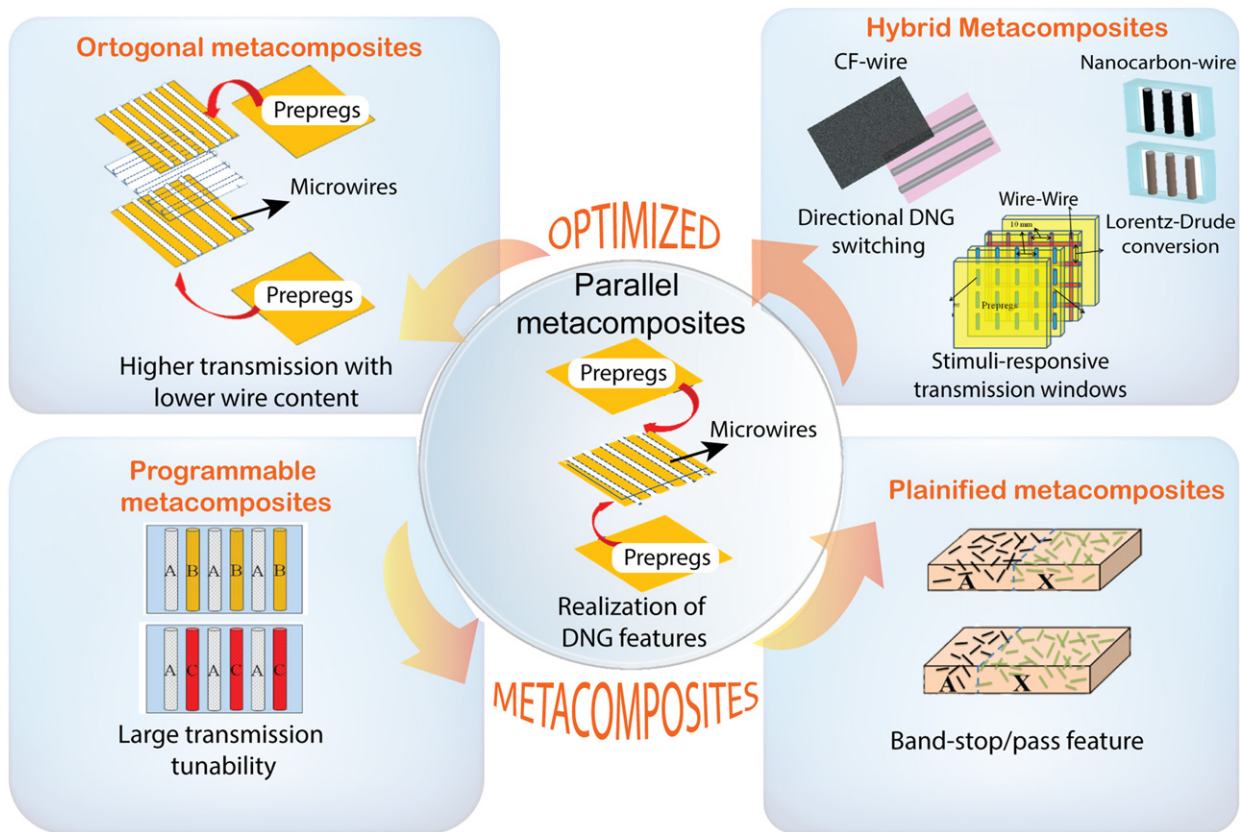


Fig. 28 Different types of microwire metacomposites obtained after optimizing the basic parallel wire configuration. Merits of each optimized metacomposite are also highlighted. Adapted from Luo, Y., Peng, H.X., Qin, F.X., *et al.*, 2014b. Metacomposite characteristics and their influential factors of polymer composites containing orthogonal ferromagnetic microwire arrays. *J. Appl. Phys.* 115, 1–6. Available at: <https://doi.org/10.1063/1.4874176Y>. Uddin, A., Estevez, D., Qin, F.X., Peng, H.X., 2020. Programmable microwire composites: From functional units to material design. *J. Phys. D Appl. Phys.* 53, 155302. Available at: <https://doi.org/10.1088/1361-6463/ab6ccd>. Uddin, A., Qin, F.X., Estevez, D., Peng, H.X., 2021. Vertical interface augmented tunability of scattering spectra in ferromagnetic microwire/silicone rubber metacomposites. *EPJ Appl. Metamater.* 8. Available at: <https://doi.org/10.1051/epjam/2021003A>. Luo, Y., Qin, F.X., Scarpa, F., *et al.*, 2016. Microwires enabled metacomposites towards microwave applications. *J. Magn. Magn. Mater.* 416, 299–308. Available at: <https://doi.org/10.1016/j.jmmm.2016.04.089>. Luo, Y., Estevez, D., Scarpa, F., *et al.*, 2019. Microwave properties of metacomposites containing carbon fibres and ferromagnetic microwires. *Research* 2019, 1–8. Available at: <https://doi.org/10.34133/2019/3239879>. Estevez, D., Qin, F., Luo, Y., *et al.*, 2019. Tunable negative permittivity in nano-carbon coated magnetic microwire polymer metacomposites. *Compos. Sci. Technol.* 171, 206–217. Available at: <https://doi.org/10.1016/j.compscitech.2018.12.016>.

sensitivity to external stimuli than their Fe-based counterparts due to their giant magneto impedance effect. On the other hand, the natural FMR of Fe-based wires facilitates negative permeability without assistance of external fields avoiding burden magnets and thus enabling device miniaturization. Regarding the influence of wire arrangement, an orthogonal array of Fe-based microwires reached higher transmission level yet with a much lower wire content compared with parallel metacomposites. This makes them attractive for miniaturized cloaking devices. The transmission tunability was further improved by designing the wire functional units through e.g., current annealing and assembling them in a specific arrangement. The concept of plainification was also applied to optimize the microwire metacomposites by rationally exploiting interfacial effects and microstructural features of randomly dispersed microwires. Remarkably, further interesting features such as DNG/band-stop behavior, directional DNG switching, and Lorentz-Drude conversion were revealed via the hybridization with different functional fillers and coatings. These results demonstrate that microwire metacomposites can potentially cover a spectrum of application areas, such as invisibility cloaking, microwave sensing, and RFID. Moreover, the microwires can be conveniently and automatically incorporated during the prepreg fabrication stage to realize microwire prepregs. Depending on application needs, microwire spacing and patterns can be tailored which is promising for the mass production of microwire metacomposites. Fig. 28 summarizes the microwire metacomposites obtained after optimizing the basic parallel wire configuration along with their EM attributes.

One outstanding issue in metacomposites containing microwires is the discrepancy between the experimental and theoretical values of f_p , which is related with the change in the microwire structure during the composite curing cycle. One possible way to address this issue would be the modification of the wires' domain structure prior to the composite fabrication through e.g., stress/current annealing (Liu *et al.*, 2012, 2014) to deliver a larger a_{eff} . Another future prospective research could be 3D metacomposites. The current scope covers thin-ply metacomposites containing one or two functional microwire layers. Thus, the EM performance

associated with the interaction between wires in the through-thickness direction is yet unclear. Ideally, we expect that a quantitative relationship can be drawn between the DNG features and the inserted microwires. Some results have been already reported in 3D nano-metamaterials (Zhao *et al.*, 2008; Wu *et al.*, 2019). However, an important consideration is that the wire amount will be therefore significantly increased, which will likely cause large reflection losses. Thus, a roadmap may be needed to carefully design wire geometry and composition to assure impedance match and minimize losses. Adopting 3D or 4D printing technology would be the most convenient and cost-effective way to manufacture such metacomposites. Moreover, the multilayer structure could not be only composed by microwires but it could also incorporate other functional fillers alternately stacked such as graphene. The microwire/matrix interfacial properties also require more detailed study. In practical applications, the microwire is assumed to be embedded in the matrix, introducing its functional capacity without dwarfing the mechanical property of the composites dramatically. The interfacial surface becomes crucial, deciding the adhesion quality between microwires and the matrix as well as the effectiveness of stress transfer. Thus, surface modification of the wires and/or polymer functionalization, as well as addition of compatibilizers may be applied. With respect to the hybrid metacomposites, EM parameters could also be manipulated by adjusting the structural features of the incorporated hybrid fibers. For instance, introducing a porous nanocarbon coating would provide a tunable nanocarbon network and accordingly tunable dielectric dispersion in the resultant composites.

Acknowledgments

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Tunneling Magnetoresistance

Atsufumi Hirohata, Department of Electronic Engineering, University of York, York, United Kingdom

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Abstract

Magnetic tunnel junctions are one of the key elements for spintronic devices, including magnetic recording, memories, and sensors. The performance of the junctions is defined by a tunneling magnetoresistance ratio and a resistance area product. These performance indicators have been increasing over the last decades. This section reviews the development and associated phenomena using spin-dependent tunneling.

Key Points

- To describe the principle of magnetic tunneling and tunneling magnetoresistance.
- To explain the mechanism of coherent tunneling.
- To discuss the use of the spin-transfer torque, spin-orbit torque and voltage controlled magnetic anisotropy in a magnetic tunnel junction.
- To review tunneling anisotropic magnetoresistance, spin torque nano-oscillation, spin filtering, resonant tunneling and granular tunneling magnetoresistance.
- To offer key materials development for the magnetic tunnel junctions.
- To provide current and future applications using magnetic tunnel junctions.

Introduction

In order to sustain the development of our modern society, many societal challenges need to be overcome, such as energy control, food security and climate change. One solution to energy control is to manage our power consumption for optimum efficiency. Such management can be achieved by introducing non-volatile highly-dense memories and highly-sensitive sensors. Current embedded memories are also based on the read-head sensors as well as Si complementary metal-oxide-semiconductor (CMOS) technologies, while current magnetic sensors have been used to detect position, angle, rotation and magnetic fields, based on three key types of technologies: Hall, anisotropic magnetoresistance (AMR) and giant magnetoresistance (GMR) effects. However, the commonly-used dynamic random memories (DRAM) requires a refreshing process due to the volatility and static random access memories (SRAM) suffers from large cell size of $\sim 130F^2$ cell size (F : fabrication rule). Similarly, currently-used sensors suffer from large temperature dependence of their output in a finite magnetic field and have limitations in their working temperature and field ranges. In order to solve these obstacles, a magnetic tunnel junction (MTJ) has been used as a memory cell and a magnetic sensor.

Tunneling Magnetoresistance

In a trilayer consisting of ferromagnet (FM)/tunnel barrier/FM, a large resistance change has been reported by switching the magnetisation of one of the FM layers (free FM) between parallel and antiparallel to the magnetisation of another ferromagnet (reference FM) as schematically shown in [Fig. 1](#). This is due to the difference in conductances of spin-polarized electrons at the Fermi level (E_F) for the first and second ferromagnets across the barrier. The change is defined as a magnetoresistance (MR) ratio as $(R_{\max} - R_{\min})/R_{\max}$, where $R_{\max}$ and $R_{\min}$ are the maximum and minimum resistance, *i.e.*, antiparallel and parallel resistance, respectively. This was first reported as 14% tunneling magnetoresistance (TMR) ratio by Jullière in Fe/GeO/Fe junction at 4.2K in 1975 ([Jullière, 1975](#)), initiating a series of studies on MR effects, such as giant magnetoresistance (GMR) in 1988 ([Baibich et al., 1988](#); [Binasch et al., 1989](#)) and Johnson transistor in 1993 ([Johnson, 1993](#)). Such magnetotransport led to spintronic research ([Wolf et al., 2001](#)), allowing these junctions to be used as a reading head in magnetic recording, magnetic random access memory (MRAM) and magnetic sensors ([Hirohata et al., 2020](#)).

Following Jullière's discovery, many other junctions have been investigated to demonstrate TMR behavior at higher temperature, *e.g.*, 2% TMR ratio at 4.2K in Ni/NiO/Co, confirming hysteretic behavior up to 77K ([Maekawa and Gärfvert, 1982](#)). Finally, TMR at room temperature (RT) was achieved using Al-O as a tunnel barrier in a coercivity difference in an Fe/Al₂O₃/Fe junction by [Miyazaki and Tezuka \(1995\)](#) and in an exchange-biased CoFe/Al₂O₃/Co junction by [Moodera et al. \(1995\)](#) independently. Since then, using a spin-valve-type structure, such as NiFe/Co/Al-O/Co/NiFe/FeMn/NiFe ([Sato and Kobayashi, 1997](#)), increasing TMR ratios were reported up to 40%–50% at RT ([Parkin et al., 1999](#)). With using an Al-O barrier but replacing a ferromagnet with Co-Fe-B, the TMR ratio has been improved very rapidly as shown in [Fig. 2\(a\)](#), resulting in the TMR ratio of 81% in a MTJ consisting of Co_{0.4}Fe_{0.4}B_{0.2}(3)/Al (0.6)-O/Co_{0.4}Fe_{0.4}B_{0.2}(2.5) (thickness in nm) at RT ([Wei et al., 2007](#)). Co_{0.4}Fe_{0.4}B_{0.2} (CoFeB) has initially been developed by IBM to promote the Frank-van der Merwe mode growth, improving the interfacial smoothness in a junction ([Hirohata et al., 2021a](#)).

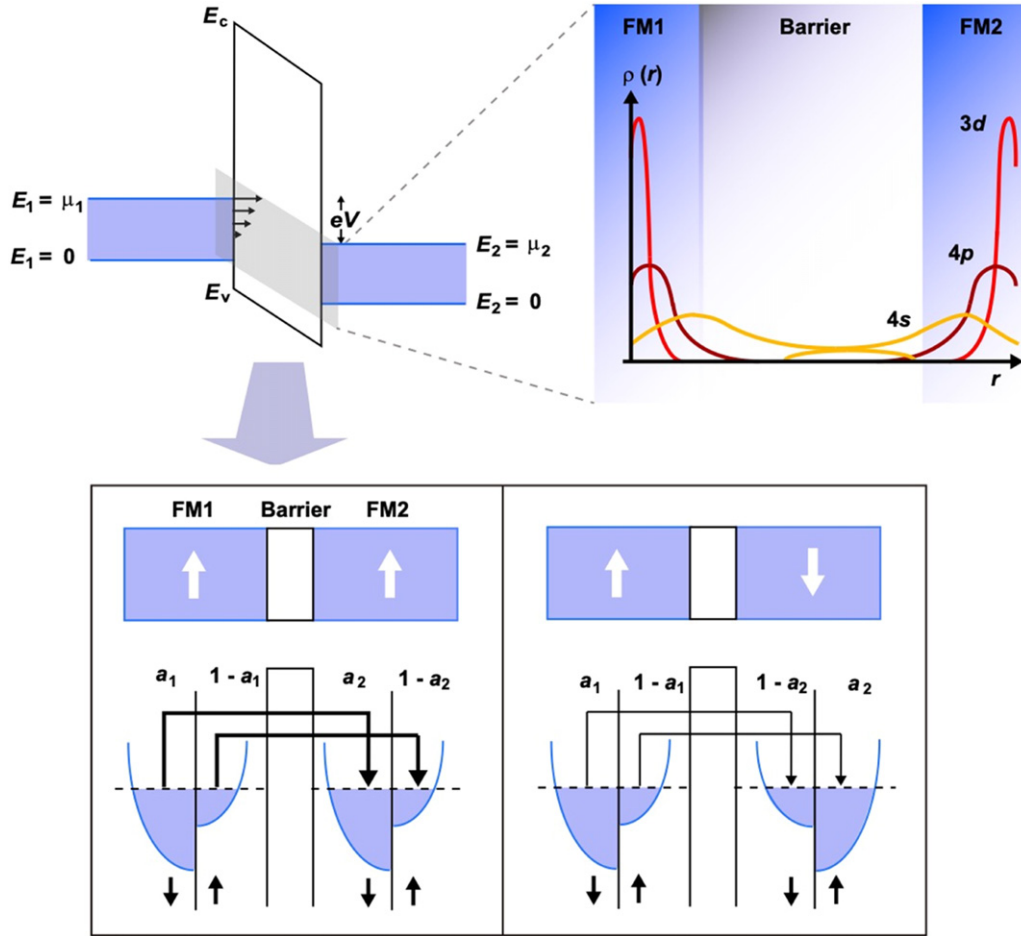


Fig. 1 Schematic diagram of spin-polarized electron tunneling. Reproduced from Hirohata, A., Yamada, K., Nakatani, Y., *et al.*, 2020. *J. Magn. Magn. Mater.* 509, 166711.

Similar interfacial dusting with an additional element has been utilized for oxide layer growth with Ti. These smooth interfaces can minimize electron scattering, leading to larger TMR ratios. In these MTJs, however, the FM/barrier interfaces may not be sharply defined and the insulators cannot be treated as an ideal barrier due to the presence of defects and grain boundaries in the barrier. Additionally, MTJs with half-metallic Co_2MnSi Heusler-alloy films as FMs have shown a large TMR ratio of 70% at RT and 159% at 2K with the resistance-area product (RA) of $10^6 \Omega \mu\text{m}^2$ (Sakuraba *et al.*, 2005). These values are the largest TMR ratios obtained in MTJs with an Al-O barrier. These results predominantly utilize spin-polarized electron tunneling in a diffusive regime.

The injection efficiency in MTJs depends not only on the spin-dependent conductance but also on the spin polarization of FMs. The TMR ratio can be defined using the spin polarization of the FM layers, *i.e.*, P_1 and P_2 for the two FM layers, FM1 and FM2, respectively, as follows (Jullière, 1975):

$$\text{TMR ratio}[\%] = 2P_1P_2/(1-P_1P_2) \quad (1)$$

P is defined by the number of majority and minority spins at E_F , N_{majority} and N_{minority} , respectively as:

$$P = \frac{N_{\text{majority}} - N_{\text{minority}}}{N_{\text{majority}} + N_{\text{minority}}} \quad (2)$$

P can be measured by replacing one of the FM layers in MTJ with a superconducting layer as Meservey and Tedrow (1994) formulated.

Using Shang's model (Shang *et al.*, 1998), effective tunneling spin polarization and interfacial spin fluctuation can be evaluated for the temperature-dependent TMR behavior as shown in Fig. 2(b).

$$G_{\text{p(ap)}} = G_0(T)[1 + (-)P_0^2m^2(T)] + G_{\text{hop}}(T), \quad (3)$$

where G_0 is the mean conductance, P_0 is the tunneling spin polarization, m is the reduced magnetisation, G_{hop} is the spin-independent conductance due to the two-step hopping *via* defect states in a tunnel barrier. G_0 , m , and G_{hop} are expressed as

$$G_0(T) = G_0 \frac{CT}{\sin CT},$$

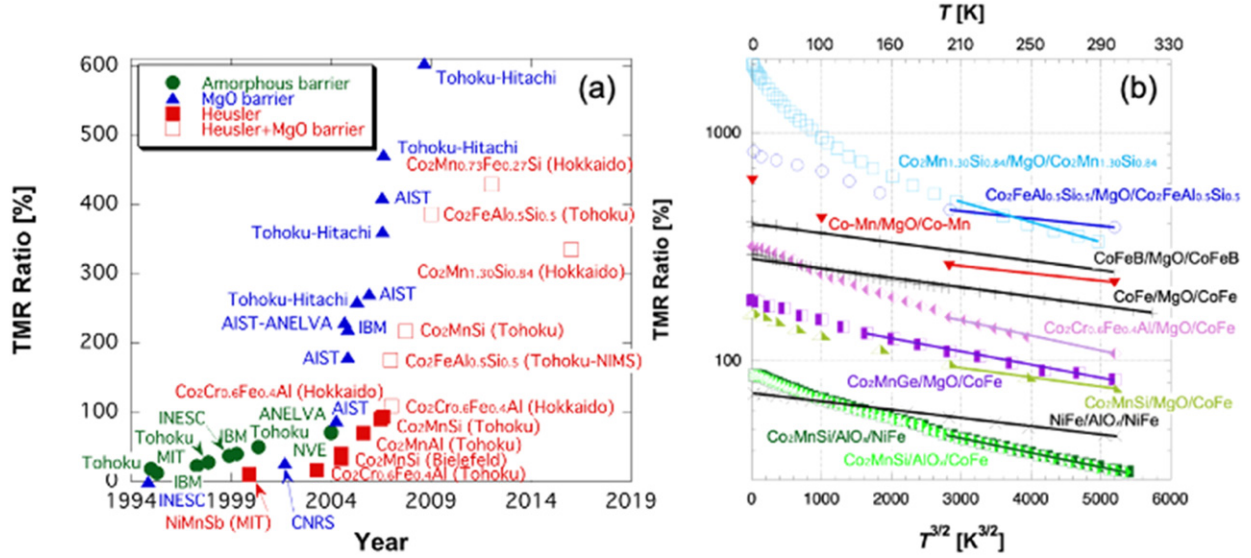


Fig. 2 (a) Recent progress in TMR ratios with different junctions. (b) Temperature dependence of TMR ratios for MTJs. Reproduced from Elphick, K., Frost, W., Samiepour, M., *et al.*, 2020. *Sci. Technol. Adv. Mater.* 22, 235.

$$m(T) = 1 - AT^{\frac{3}{2}},$$

$$G_{\text{hop}}(T) = BT^{\frac{4}{3}},$$

where A is the parameter characterising spin fluctuation at the interface between FM and the barrier. C is $1.387 \times 10^{-3} d / \sqrt{\phi}$ with the barrier width d in nm and height ϕ in eV. B and G_0 are constants. The spin-dependent and -independent parts of the conductance, $\bar{G}$ and ΔG , respectively, can be defined as follows:

$$\bar{G} = \frac{G_p + G_{\text{ap}}}{2} = G_0(T) + G_{\text{hop}}(T), \quad (4)$$

$$\Delta G = \frac{G_p - G_{\text{ap}}}{2} = G_0(T) P_0^2 m^2(T). \quad (5)$$

Using Eqs. (2) and (3), a TMR ratio satisfies the following relationship:

$$\text{TMR ratio [\%]} = \frac{2\Delta G}{G_{\text{ap}}} \times 100. \quad (6)$$

By measuring current-voltage (I - V) characteristics of MTJ, the height and width of the tunnel barrier can be estimated with Simmons (1963) fitting.

Additionally, an electromotive force (EMF) has been theoretically predicted from Faraday's law by Barnes and Maekawa (2007), which becomes dominant for time-dependent magnetisation, *e.g.*, magnetic domain-wall motion. Their prediction has been proven experimentally in MTJ, consisting of GaAs/zinc-blende MnAs nanoparticles/GaAs (Hai *et al.*, 2009). Here, EMF is found to work on a timescale of $10^2 \sim 10^3$ s, which controls the spin-dependent tunneling behavior in the superparamagnetic MnAs nanoparticles, achieving a very large MR ratio of up to 100,000% at 3K.

Coherent Tunneling

By replacing amorphous Al-O with epitaxial MgO, over 1,000% TMR ratios have been theoretically predicted due to coherent tunneling at an Fe/MgO interface (Butler *et al.*, 2001; Mathon and Umerski, 2001). At an Fe/MgO (and CoFeB/MgO as later discovered) interface, their Δ_1 bands are calculated to be connected but the other bands, *e.g.*, Δ_2 and Δ_5 are not. Since the Δ_1 band is 100% spin-polarized in Fe and CoFe alloys, the corresponding electrons tunnel through the MgO barrier half-metallically. For such coherent tunneling, effective P can become 100%, leading to an infinite TMR ratio.

Experimentally, giant TMR ratios of $> 100\%$ at RT have been reported by Parkin *et al.* (2004) and Yuasa *et al.* (2004) independently. They used epitaxial MTJ, which was achieved by annealing during/after the deposition, promoting the crystallization of initially amorphous Fe (CoFe)/MgO/Fe (CoFe) trilayer. Accordingly, a TMR ratio as large as 604% has been demonstrated in MTJ consisting of Co_{0.2}Fe_{0.6}B_{0.2} (6)/MgO (2.1)/Co_{0.2}Fe_{0.6}B_{0.2} (4) (thickness in nm) at RT (Ikeda *et al.*, 2008). As the crystallization is typically initiated by MgO, their softness of lattice constants and robustness against crystalline orientations can maintain coherent tunneling (Elphick *et al.*, 2021). The interfacial lattice matching has been improved by controlling the lattice constant of MgO by Al doping, achieving TMR ratios of 342% at RT (616% at 4K) with RA of $2.5 \times 10^3 \Omega \mu\text{m}^2$ in

MTJs with B2-Co₂FeAl as FMs (Scheike *et al.*, 2016). For further increase in the TMR ratios, a half-metallic Heusler alloy has been used as FMs in MTJs. For example, MTJs consisting of Co₂Mn_{0.73}Fe_{0.27}Si/MgO/Co₂Mn_{0.73}Fe_{0.27}Si shows the TMR ratio of 429% at RT (2,610% at 4K) with RA of $7 \times 10^7 \Omega \mu\text{m}^2$ (Liu *et al.*, 2015), which is the largest TMR ratio reported in a Heusler-alloy-based MTJ to date. Such strong temperature dependence in the TMR ratios may be due to the interfacial spin fluctuation according to Shang's model.

Spin-Transfer Torque Switching

A TMR nanopillar with an Al-O barrier has then been employed for current-induced magnetisation switching by spin-transfer torque (STT), showing a TMR ratio of $\sim 30\%$ and the switching current density J_c of $\leq 10^7 \text{ A/cm}^2$ at RT (Fuchs *et al.*, 2004). After the discovery of coherent tunneling, improved operation of a TMR nanopillar has been demonstrated with a TMR ratio of $\sim 100\%$ and J_c of $\sim 6 \times 10^6 \text{ A/cm}^2$ with a pulsed current of 100 ms duration (Kubota *et al.*, 2005), followed by a further improvement with a TMR ratio of 160% and J_c of $2.5 \times 10^6 \text{ A/cm}^2$ at RT (Hayakawa *et al.*, 2005).

STT can be described as $\frac{\gamma}{d} \vec{m} \times (\vec{m} \times \Delta \vec{J}_s)$ ($\vec{m}$: the unit vector of the magnetisation) (Slonczewski, 1996; Berger, 1996). By adding this term to the Landau-Lifshitz-Gilbert (LLG) equation (Landau and Lifshitz, 1935; Gilbert, 2004), the magnetisation dynamics can be explained using the Landau-Lifshitz-Gilbert-Slonczewski equation:

$$\frac{d\vec{M}}{dt} = -\gamma \vec{m} \times \vec{H}_{\text{eff}} + \alpha \vec{m} \times \frac{d\vec{m}}{dt} - \frac{\gamma}{d} \vec{m} \times (\vec{m} \times \Delta \vec{J}_s). \quad (7)$$

Here, the second term is the relaxation term with the Gilbert damping constant α . This term increases with increasing temperature as described by the *s-d* scattering model (Mott and Massey, 1965). Conduction electrons (*s*) are scattered by localized spins (*d*) during the spin relaxation process, releasing the corresponding momentum into the lattice via the spin-orbit interaction at high temperature, *i.e.*, α , to be proportional to the resistivity of the system ρ (resistivity like). At low temperature, α is proportional to the conductivity of the system σ (conductivity like) (Hirohata and Takanashi, 2014).

The spin relaxation time τ can be estimated using the D'yakonov-Perel model, $1/\tau \sim \omega^2 \tau_p$ (for large electron scattering probabilities (D'yakonov and Perel, 1972)) or the Elliott-Yaffet model: $1/\tau \propto 1/\tau_p$ (for strong spin-orbit interactions (Elliott, 1954; Yafet, 1963)), where ω is the Lamor frequency and τ_p is the momentum relaxation time of an electron. To describe the conductivity-like damping at low temperature, the breathing Fermi surface model has been proposed (Kambersky, 1970b; Koreman and Prange, 1972; Kuneš and Kambersky, 2002). For a spin-polarized electrical current, STT is antiparallel to the Gilbert damping torque. Eq. (7) indicates that the increase in the spin current $\vec{J}_s$ reduces the relaxation, leading to the precessional motion of magnetisation yielding magnetisation switching or steady-state spin-torque oscillation.

Spintronic Device Applications

MTJs have been implemented as a read head in a hard disk drive (HDD) by Seagate in 2004. Since then, MTJ heads have been reducing the bit size in perpendicular magnetic recording, achieving the areal density of $> 600 \text{ Gbit/in}^2$ (Hirohata *et al.*, 2021b). For further development above 2 Tbit/in^2 as summarized in Fig. 3, it becomes increasingly difficult to use MgO-based MTJs since the barrier thickness becomes ultrathin (below 1 nm), which impacts its reliability, yields and reduces the corresponding TMR ratios.

MTJ has also been used as a MRAM cell, the latest of which uses perpendicularly magnetized MTJs for STT-MRAM, it was proposed to increase the effective anisotropy by benefiting from perpendicular magnetic shape anisotropy (Watanabe *et al.*, 2018; Perrissin *et al.*, 2018). The anisotropy stability factor Δ ($= E / k_B T$) can be enhanced thanks to the combined influence of the interfacial anisotropy at the magnetic electrode/MgO interface (Ikeda *et al.*, 2010), (Dieny and Chshiev, 2017) and of the vertical shape anisotropy. In order to promote MRAM as a viable solution for embedded memory and/or static random access memory (SRAM) replacement, two technologies for next-generation MRAMs have been proposed: spin-orbit torque (SOT) and voltage-controlled magnetic anisotropy (VCMA) to reduce the operation time and power consumption.

Spin-Orbit Torque

The spin-orbit interaction (SOI) can be determined as

$$H_{\text{SOI}} = \eta_{\text{SO}} \vec{s} \cdot \vec{L}, \quad (8)$$

where η_{SO} is the spin-orbit interaction constant, $\vec{s}$ and $\vec{L}$ are the spin and orbital moments. η_{SO} is determined as

$$\eta_{\text{SO}} = -(g-1) \frac{q\hbar^2}{2m^2c^2} \left(\frac{1}{r} \frac{d\phi(r)}{dr} \right) \quad (9)$$

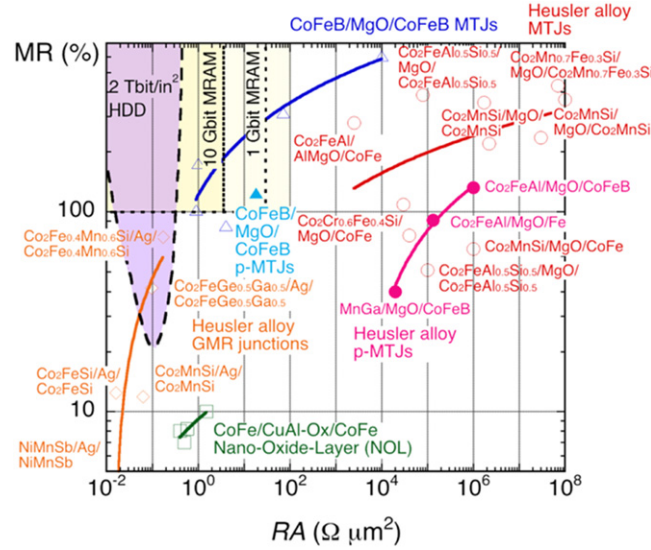


Fig. 3 Relationship between a MR ratio and RA of MTJs with CoFeB/MgO/CoFeB (blue triangles), nano-oxide layers (NOL, green squares) and Heusler alloys (red circles) with in-plane (open symbols) and perpendicular magnetic anisotropy (closed symbols) together with that of GMR junctions with Heusler alloys (orange rhombus). The target requirements for 2 Tbit/in² HDD read heads as well as 1 and 10 Gbit MRAM applications are shown as purple and yellow shaded regions, respectively. Reproduced from Hirohata, A., Yamada, K., Nakatani, Y., *et al.*, 2020. J. Magn. Magn. Mater. 509, 166711.

Here, g is the Lande g -factor, q is the electron charge, $\hbar$ is the Planck constant divided by 2π , m is the electron mass, c is the speed of light, $\phi(r)$ is the scalar potential.

SOI can induce SOT in FM/heavy metal (HM) bilayers by flowing an in-plane electrical current. The magnitude of SOT can be evaluated by the magnetisation switching as similar to STT. For the perpendicular magnetisation, J_c is estimated to be $(2.0 \pm 0.1) \times 10^{10}$ A/m with the θ_{SH} of (-0.25 ± 0.02) . For the in-plane magnetisation perpendicular to the electrical current direction, J_c is reduced to 1.0×10^{10} A/m with the θ_{SH} of -0.08 , while for the in-plane magnetisation parallel to the current, J_c is also reduced to $(4.3 \pm 0.2) \times 10^{10}$ A/m with the θ_{SH} of (-0.22 ± 0.01) , which has the fast-damping process (Fukami *et al.*, 2016).

Voltage Controlled Magnetism

Ohno *et al.* (2000) have achieved a phase transition between ferromagnetism and paramagnetism by applying a bias voltage (± 125 V) on an InMnAs layer at 25K. Offering fully electrical control of spintronic devices. A similar control in magnetic behavior has been demonstrated in FePd (Koo *et al.*, 2009) as well as an ultrathin Co film (Weisheit *et al.*, 2007). For a sample, consisting of a 0.4 nm thick Co layer, $+10$ V (± 2 MV/cm²) induces FM but -10 V induces non-magnetism (NM).

Accordingly, voltage-controlled magnetic anisotropy (VCMA) has been implemented in MTJs in the view of zero standby power and ultralow active power consumption (Nozaki *et al.*, 2017). In a Cr (30)/Fe (1.0)/Ir (0.05)/MgO (2.5) (thickness in nm) junction, a large interfacial perpendicular anisotropy up to 3.7 mJ/m² was achieved, which is 1.8 times larger than that of the pure Fe/MgO interface. The VCMA coefficient is reported to be up to 320 fJ·V/m as well as high-speed response. For MRAM implementation, the VCMA coefficient of 1000 fJ V/m may be needed.

Tunneling Anisotropic Magnetoresistance

For a junction consisting of a FM/tunneling barrier/NM, the resistance can be controlled by magnetisation rotation through the SOT at the interface, *i.e.*, tunneling anisotropic magnetoresistance (TAMR). This effect has first been demonstrated experimentally by Gould *et al.* (2004) in a junction of Ga_{0.94}Mn_{0.06}As (70)/AlOx (1.4)/Ti (5)/Au (300) (thickness in nm). A TAMR ratio of $\sim 0.4\%$ has also been measured with GaAs as a tunnel barrier (Moser *et al.*, 2007). Further increase in TAMR to 13% has been reported for a textured Co (1)/Pt (1)/Co (1)/Pt (0.5)/Al-O (2)/Pt (5) (thickness in nm) junction with perpendicular magnetic anisotropy (Park *et al.*, 2008). TAMRs have been reported to be dependent strongly on the crystalline structure of the tunneling barrier (Gao *et al.*, 2007). By replacing an amorphous Al-O barrier with highly-textured MgO in MTJs of Co_{0.49}Fe_{0.21}B_{0.30}/Co_{0.70}Fe_{0.30}/Oxide/Co_{0.70}Fe_{0.30}/Co_{0.49}Fe_{0.21}B_{0.30}, the TMR ratios have been increased from 89% to 377% at 10K (Park *et al.*, 2011).

Spin Torque Nano-Oscillation

Microwave generation has been reported in a Co/Cu/Co GMR nanopillar by STT by Kiselev *et al.* (2003). Accordingly, a MgO-based MTJ has been used to demonstrate 140 nW oscillation (Deac *et al.*, 2008). Such MTJs have been used as a spin-torque nano-oscillator (STNO). A critical parameter of STNO is the Q-factor, which depends on the TMR ratio, junction resistance, a bias voltage and an oscillation angle. The above MgO-based MTJ shows the Q-factor of ~ 5 , indicating multiple oscillation may be induced in the nanopillar. GMR nanocontacts, on the other hand, can handle a large bias voltage, leading to the Q-factor of up to 18,000 at the oscillation frequency of 34 GHz (Rippard *et al.*, 2004). However, the oscillation power is only 1 nW. Using a perpendicularly-magnetized free layer, the Q-factor of MTJ has been reported to be 135 with maintaining 550 nW oscillation (Kubota *et al.*, 2013). For a device application, the Q-factor and oscillation power needs to be over 100 and 1 μ W, respectively. Recently, a sombrero-shaped STNO has been used for the spin-torque oscillation with achieving the maximum Q-factor of 3,200 and 2.4 μ W (Maehara *et al.*, 2014).

SOT can also induce its oscillatory behavior (Ramaswamy *et al.*, 2018; Manchon *et al.*, 2019). Note that SOT is known to be more efficient and faster than STT by almost one order of magnitude. SOT oscillations have been reported in MTJs of CoFeB/MgO/CoFeB, generating 1.6 $\sim$ 1.8 GHz oscillation under a magnetic field application of $\sim$ 160 Oe (Liu *et al.*, 2012). Subsequently, higher oscillation of $\sim$ 7.5 GHz has been achieved by introducing an electrical current into a micron-size disc of NiFe (5)/Pt (8) (thickness in nm) (Demidov *et al.*, 2012). Auto-oscillation can be efficiently synchronised in a disc of Py (5)/Pt (8) (thickness in nm) using an external frequency equal to twice that of the auto-oscillations (Demidov *et al.*, 2014). SOT is characterized a strong increase of the oscillation linewidth with temperature, which is correlated with the emergence of an additional higher-frequency oscillation mode (Liu *et al.*, 2013).

Spin Filtering and Resonant Tunneling

Similar to the coherent tunneling, a spin-filtering layer, which preferentially flows one of the spin-polarized electrons, has successfully produced very large TMR ratios *via* large Zeeman splitting in magnetic semiconductors, *e.g.*, EuO and EuS (Moodera and Meservey, 2004). Larger TMR ratios have been reported using coherent tunneling with a MgO barrier, of which lattice matching can be precisely controlled by Al doping (LeClair *et al.*, 2002).

Recently, a resonant tunneling junction through a quantum-well (QW) state has been proposed by forming a double tunneling barrier made of Mg-Al-O, *i.e.*, double MTJ, and has demonstrated the corresponding TMR oscillation for the FM layer thickness up to 12 nm (Tao *et al.*, 2015). A double MTJ and QW has also shown quantum resonant tunneling up to the FM thickness of 10 nm (Tao *et al.*, 2019).

Neuromorphic Logic

Nanoelectronic devices, namely silicon chips, have been following Moore's law by increasing the number of transistors on a chip over the last decades (Dieny *et al.*, 2020). Beyond von-Neumann computation, one of the solutions is neuromorphic computing to mimic a brain, where a neuron only sends a signal when a spike input to the neuron exceeds a threshold. Since the pioneering work on neuromorphic computing by Mead of the California Institute of Technology in 1980, many researchers have been investigating new architectures and scaling up the number of their artificial synapses. For example, Biocomp (See "Relevant Websites section") utilizes voltage-tuneable nano-resistance in MTJ, which has also been studied by Tohoku University (Borders *et al.*, 2016). Their concept is to utilize resistance changes in a STT-induced magnetisation reversal process and to control their "minor" loops. The data is stored as a magnetisation direction in a free FM layer in an MTJ, which can be reversed by applying a current. Phase-synchronisation of a vortex-type STNO array has also been demonstrated (Tsunegi *et al.*, 2018). Up to 8 STNOs are used to demonstrate long-term stability of the phase difference better than 1.6 ms and the noise power spectral density of phase difference of $\sim$ 80 dBc/Hz at 1 kHz offset frequency.

Recently, probabilistic magnetisation reversal has also been used for stochastic computation (Borders *et al.*, 2019). An array of MTJs consisting of CoFeB/MgO/CoFeB has been employed for the factorization of integers up to 945. Similar chaotic behavior has been reported in a vortex oscillator with a nano-contact up to 1.5 GHz (Devolder *et al.*). Such a computational method can bridge between the conventional and quantum computations with low energy consumption.

Low Damping and Anisotropic Materials

For faster magnetisation reversal in MTJs, especially as data bits of MRAMs, a low damping constant α is required, achieving smaller J_c . To date, Ni_{0.8}Fe_{0.2} has been used as a low damping material, while the other materials, *e.g.*, Heusler alloys, have been developed as shown in Fig. 4 for further reduction in their Gilbert damping constant α . Theoretically, α is known to be proportional to the density of states (DOS) at E_F (Kambersky, 1970a), suggesting the half-metallic ferromagnets to exhibit a smaller α .

A CoFeB/MgO/CoFeB MTJ has been widely used to induce perpendicular anisotropy (Manchon *et al.*, 2008). The CoFeB/MgO interface induces interfacial hybridization between the electronic orbitals of the transition metals and those of the oxygen in the adjacent oxide layer. For further miniaturization of MTJ (typically sub-50 nm in diameter), it is critical to use perpendicularly anisotropic FMs. A reference FM layer in MTJs needs to have a high Gilbert damping, while a free FM layer must exhibit a low Gilbert damping for STT-MRAM and spin-torque oscillators to minimize their power consumption. Highly perpendicularly anisotropic

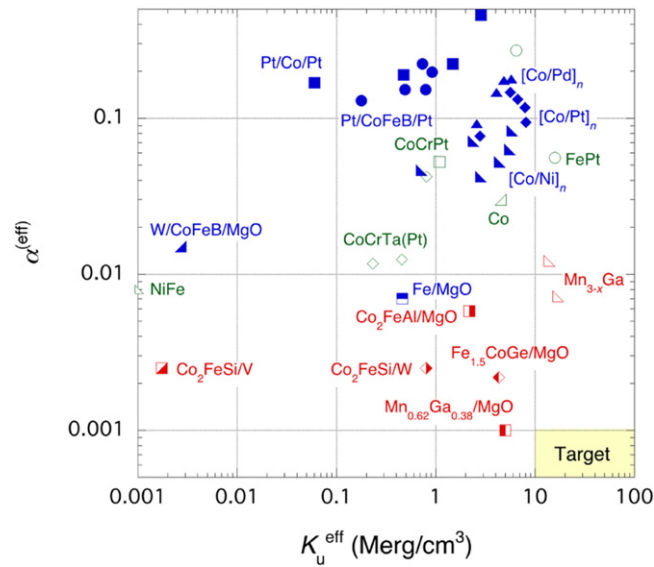


Fig. 4 Relationship between the magnetic anisotropy constant K_u^{eff} and the Gilbert damping constant α . Single films, multilayers with heavy metals and half-metallic Heusler alloy films are shown in green open, blue closed and red open symbols. Heusler alloys with MgO and heavy metals are also shown in half-closed symbols. Reproduced from Hirohata, A., Yamada, K., Nakatani, Y., *et al.*, 2020. J. Magn. Mater. 509, 166711.

materials with large damping can be generally realised by using materials with large spin orbit constant, typically Pt, Ir and Au. Such materials are in the upper right corner of Fig. 4, such as [Co/Pt] or [Co/Pd] multilayers or alloys and $L1_0$ -ordered FePt alloys.

Intense research on such low-damping and highly-anisotropic materials is ongoing. For instance, MTJs consisting of Co_2FeAl (1.2)/MgO (1.8)/Fe (0.1)/CoFeB (1.3) (thickness in nm) have been reported to show TMR of 132% and RA of $1 \times 10^6 \Omega \mu\text{m}^2$ at RT (Wen *et al.*, 2014). A perpendicularly magnetized seed layer has also been used to induce interfacial exchange interactions, *e.g.*, MTJs of $L1_0$ -CoPt/Co₂MnSi/MgO/FePt (Hiratsuka *et al.*, 2010). A W(110) seed layer has also been reported to induce perpendicular magnetic anisotropy in a $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ Heusler alloy layer (Frost *et al.*, 2019).

Granular Tunneling Magnetoresistance

TMR has also been measured in a granular system with FM nanoparticles dispersed in an insulating matrix. The first granular TMR effect was observed in a granular Ni-SiO₂ film (Gittleman *et al.*, 1972) with the TMR ratio of about 1% at 300K. Fujimori *et al.* (1995) reported the TMR ratio of 8% at RT in a Co-Al-O system. The signals contain the conventional TMR effect with an additional charging effect in the nanoparticles. A significant enhancement in the TMR ratio of more than 20% at 2K has then been reported (Mitani *et al.*, 1998). This agrees with the enhancement by $2/(1 - P^2)$ as theoretically proposed by co-tunneling across nanoparticles in the Coulomb blockade regime (Takahashi and Maekawa, 1998).

By inserting such a granular TMR system into an insulating layer in a conventional MTJ, Schelp *et al.* successfully fabricated a double MTJ (Schelp *et al.*, 1997). They sandwiched Co nanoparticles of 2~4 nm diameter dispersed in Al-O between Co FM layers, achieving the TMR ratio of approximately 15% at 4.2K and 10% at RT. Significant enhancement of the TMR ratios has then been reported in a double MTJ of CoFe/CoFe:Al-O/CoFe (Sukegawa *et al.*, 2005). The Coulomb blockade was observed below 50K for CoFe nanoparticles with diameters between 2.0 and 4.5 nm. The bias-voltage-dependence of the TMR ratios increased from 10.5% at 20 mV at 7K to 23.9% at 0.60 mV, which agrees very well with the Takahashi-Maekawa theory near zero bias (Takahashi and Maekawa, 1998).

Granular Tunneling Magnetoresistance

Interfacial spin transport in MTJs can also be improved using layered two-dimensional (2D) materials connected *via* the van der Waals force without chemical bonding (Piquemal-Banci *et al.*, 2017; Zhang *et al.*, 2021). For example, a graphene sheet has been used as a tunnel barrier, forming a Co/graphene/NiFe MTJ (Cobas *et al.*, 2012). The corresponding TMR ratio was reported to be 2% at 4K (~0.4% at RT). Chemical vapor deposition was then used to grow hexagonal boron nitride (h-BN) as a tunnel barrier between Co and Fe layers, achieving 6% TMR ratio at RT (Piquemal-Banci *et al.*, 2016). Transition metal dichalcogenides (TMDs) have also been used as a barrier, of which electronic properties depend on the layer thickness. NiFe/MoS₂/NiFe for example showed 0.73% TMR ratio at 20K (Wang *et al.*, 2015).

Using a 2D material as FM layers in addition to a tunnel barrier, band matching was theoretically predicted to achieve over 700% and 3600% TMR ratios in MnSe₂/h-BN/MnSe₂ (Pan *et al.*, 2019) and CrI₃/h-BN/CrI₃ (Yan *et al.*, 2020) MTJs according to *ab initio* calculations. Experimentally, TMR ratio of 8000% was measured at 10K for a graphene/CrI₃/graphene junction

(Wang *et al.*, 2018a). Fe₃GeTe₂ has also been investigated as FM layers in MTJs (Li *et al.*, 2019), experimentally achieving a TMR ratio of 180% was reported at 4.2K (Wang *et al.*, 2018b).

Outlook

The importance of MTJs has been significantly increasing recently. Their properties can be evaluated by their TMR ratios, RAs , K_u^{eff} and α . Depending on their applications, the requirements for these four parameters can be varied. For example, for the development of non-volatile memories, MTJs with large TMR ratios with small RAs , large K_u^{eff} as well as large and small α for reference and free FM layers, respectively. These MTJs can be switched efficiently by SOT or VCMA by integrating a large SOI material or multiferroic seed layer, respectively. Insertion of a 2D material can also improve the interfacial quality to reduce the unwanted spin scattering. These MTJs can also be used for unconventional computing, *e.g.*, stochastic, and neuromorphic computing. For the sensor applications, MTJs can offer increased sensitivity, reduced temperature dependence and broader field dynamics, which can be ideal for magnetic recording and medical applications. Based on the development of new materials, improvement in the interfacial quality, and elimination of edge roughness and domains, these next-generation devices will contribute to the sustainable development of our society in terms of their low-power consumption and highly-efficient operation.

Acknowledgments

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<https://gdr-biocomp.fr/en/>.
BioComp.

Curvilinear Magnetism

Denis D Sheka, Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

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Abstract

Curved magnetic architectures are key enablers of the prospective magnetic devices with respect to size, functionality and speed. By exploring geometry-governed magnetic interactions, curvilinear magnetism offers a number of intriguing effects in curved magnetic wires and curved magnetic films. The aim of this article is to summarize recent developments and current challenges in theory, fabrication, and characterization of curvilinear magnetic nanostructures. Prospective research directions and applications of curvilinear magnetism are discussed.

Nomenclature

1D	one-dimensional.
2D	two-dimensional.
3D	three-dimensional.
BLS	Brillouin light scattering.
DMI	Dzyaloshinskii-Moriya interaction.
EBL	Electron beam lithography.
e-skins	electron skin.
FEBID	Focused electron beam induced deposition.
GLAD	Glancing angle deposition.
GMR	Giant magnetoresistance.
m-MEMS	Magnetic microelectromechanical system.
MOKE	Magneto-optical Kerr effect.
NSL	Nanosphere lithography.
NV	nitrogen-vacancy.
SQUID	superconducting quantum interference device.
STEM	Scanning transmission electron microscopy.
TEM	Transmission electron microscopy.
TPL	Two-photon lithography.
XMCD	X-ray magnetic circular dichroism.
XMLD	X-ray magnetic linear dichroism.
XPEEM	X-ray photoemission electron microscopy.
MTXM	Magnetic transmission soft X-ray microscopy.
spin-SEM	Spin-polarized scanning electron microscopy.
STXM	Scanning transmission X-ray microscopy.
A	exchange stiffness.
D_{ijk}	constants of Dzyaloshinskii-Moriya interaction.
$\mathbf{e}_{1,2}^{\text{an}}$	anisotropy axes.
E_A	energy of effective anisotropy.
E^{an}	magneto-crystalline anisotropy.
E^{DMI}	energy of Dzyaloshinskii-Moriya interaction.
E_{mD}	energy of mesoscale DMI.
E^{ms}	magnetostatic energy.
$E_{\text{ms}}^{\text{curv}}$	curvature contribution to the magnetostatic energy.
$E_{\text{ms}}^{\text{shape}}$	shape contribution to the magnetostatic energy.
E^{x}	exchange energy.
$\mathcal{F}_{\alpha\beta}$	Frenet-Serret tensor.
g	geometrical charge.
$m; 210B;$	mean curvature.
$K_{1,2}$	anisotropy constants.
$\mathcal{K}_{\alpha\beta}$	coefficients of geometry-induced anisotropy.
$\hat{\mathbf{n}}$	surface normal.
κ	curvature of the wire.
κ_1 and κ_2	curvatures of the surface.
$L_{ij}^{(k)}$	Lifshitz invariants.

$\mathbf{m}$	normalized magnetization.
$\mathbf{M}$	magnetization.
M_s	saturation magnetization.
ρ	tangential charge.
τ	torsion of the wire.
∂_ν	tangential derivatives.

Introduction

The onrush of nanotechnologies extended conventional flat architectures to curved space, showcasing the fundamental importance of the mutual interplay between geometry, topology and the order parameter. In magnetism, fundamental and applied research of curved magnetic nanoarchitectures and related geometry-governed effects are united in curvilinear magnetism (Streubel *et al.*, 2016). This field provides a framework to understand the behavior of a curved low-dimensional system and tailor its responses to external stimuli. Being truly multifaceted research field, curvilinear magnetism strongly contributes to nanomagnetism (Streubel *et al.*, 2016), shapeable magnetoelectronics (Makarov *et al.*, 2016; Kamaushenko *et al.*, 2019), spintronics (Streubel *et al.*, 2016; Fischer *et al.*, 2020), spin-orbitronics (Han *et al.*, 2021; Go *et al.*, 2021), skyrmionics (Dohi *et al.*, 2021; Liu *et al.*, 2022), 3D magnonics (Gubbiotti, 2019; Barman *et al.*, 2021), magnetic sensorics (Melzer *et al.*, 2020), flexible magnonics (Faurie *et al.*, 2021) microrobotics (Sitti, 2017; Alapan *et al.*, 2019). It benefits and also motivates the further development of modern fabrication and characterization methods (Streubel *et al.*, 2016; Fernández-Pacheco *et al.*, 2017; Fischer *et al.*, 2020). The current and future challenges of curvilinear magnetism are outlined in the 2017 (Sander *et al.*, 2017) and 2020 (Vedmedenko *et al.*, 2020) Magnetism Roadmaps and perspective papers (Sheka, 2021; Streubel *et al.*, 2021). Different aspects of magnetism in curved geometries, 3D nanomagnetism are comprehensively elaborated in the book (Makarov and Sheka, 2022), and review articles (Makarov *et al.*, 2022; Sheka *et al.*, 2022a).

Fundamentals

By tailoring curvature and topology of conventional magnetic materials there appears a possibility to control material response leading to modification or even launching new functionalities (Streubel *et al.*, 2016; Fernández-Pacheco *et al.*, 2017; Fischer *et al.*, 2020). All these new material properties became a reality due to curvature-induced effects, which are stemming from the geometry-governed magnetic interactions caused by the local and global properties of the object's geometry. The phenomenological description of magnetization statics and dynamics in the continuum limit relies on the total energy of the magnet which can include different contributions. Let us focus on a classical uniaxial ferromagnet with the following energy functional $E = E^x + E^{\text{an}} + E^{\text{DMI}} + E^{\text{ms}}$. The first term is the exchange energy (Hubert and Schäfer, 2009): $E^x = -A \int d\mathbf{r} (\mathbf{m} \cdot \nabla^2 \mathbf{m})$ with A being the exchange stiffness, $\mathbf{m} = \mathbf{M}/M_s$ being the normalized magnetization, and M_s being the saturation magnetization. The next term is the magneto-crystalline anisotropy (Coe, 2001; Hubert and Schäfer, 2009); in the case of biaxial anisotropy, the corresponding energy $E^{\text{an}} = \int d\mathbf{r} [K_1 (\mathbf{m} \cdot \mathbf{e}_{1,2}^{\text{an}})^2 + K_2 (\mathbf{m} \cdot \mathbf{e}_2^{\text{an}})^2]$ with $K_{1,2}$ being the anisotropy constants and $\mathbf{e}_{1,2}^{\text{an}}$ being the anisotropy axes. When $|K_1| > |K_2|$, the direction $\mathbf{e}_{1,2}^{\text{an}}$ is called the principal easy (hard) axis for $K_1 < 0$ ($K_1 > 0$), respectively. Chiral properties of magnets are typically determined by the intrinsic Dzyaloshinskii-Moriya interaction (DMI) (Dzyaloshinsky, 1958; Moriya, 1960) composed of Lifshitz invariants $L_{ij}^{(k)} = m_i \partial_k m_j - m_j \partial_k m_i$ (Dzyaloshinskii, 1964). The DMI energy $E^{\text{DMI}} = \int d\mathbf{r} D_{ijk} L_{ij}^{(k)}$ with D_{ijk} being the DMI constants; here and below Latin indices refer to the Cartesian reference frame of the ambient space, and the Einstein summation convention is used. All above terms are local. Besides, in many practical cases it is important to take into account the nonlocal magnetostatic interaction. Its energy density reads (Hubert and Schäfer, 2009) $E^{\text{ms}} = \frac{1}{2} M_s^2 \int d\mathbf{r} \int d\mathbf{r}' (\mathbf{m}(\mathbf{r}) \cdot \nabla)(\mathbf{m}(\mathbf{r}') \cdot \nabla') |\mathbf{r} - \mathbf{r}'|^{-1}$.

At present the anisotropy is the mainly discussed source of the geometry-governed magnetic interactions. Other important sources include: spin-polarized currents with spin-orbit torques in the Landau-Lifshitz equation, which feel the geometry, and magnetoelastic nanomagnets, where elastic and magnetic energies become coupled being sensitive to the curved geometry. When discussing the anisotropy, we can distinguish two most important contributions of geometry-governed interactions. The first one is the magneto-crystalline anisotropy directions $\mathbf{e}_{1,2}^{\text{an}}$ in curved magnets, which are determined by the spatial variation of the anisotropy axis $\mathbf{e}_{1,2}^{\text{an}} = \mathbf{e}_{1,2}^{\text{an}}(\mathbf{r})$, following the sample geometry. In particular, the principle anisotropy axis direction of the narrow curved wire is typically tangential to the wire, while $\mathbf{e}_1^{\text{an}}$ is directed along the surface normal $\hat{\mathbf{n}}$ for curved films (Makarov *et al.*, 2007; Smith *et al.*, 2011; Ball *et al.*, 2014). The second contribution is the magnetostatic interaction in thin curved nanoobjects, which results in a shape anisotropy with the principle anisotropy direction $\mathbf{e}_1^{\text{an}}$ following the sample geometry, similar to the magneto-crystalline anisotropy. Such a reduction of the nonlocal interaction to the local anisotropy was rigorously derived for curved wires (Slastikov and Sonnenberg, 2012), ribbons (Gaididei *et al.*, 2017), shells (Slastikov, 2005; Fratta *et al.*, 2020) and films (Fratta, 2020).

Emergent Interactions

The current description of the curvature-induced effects is based on a micromagnetic framework of curvilinear magnetism (Gaididei *et al.*, 2014; Sheka *et al.*, 2020). The geometrically broken symmetry allows to systematize geometrical effects by restructuring all magnetic energy terms according to their local spatial symmetry. By representing the magnetic subsystem in a

curvilinear reference frame, which follows the sample geometry (the Frenet trihedron in case of the curved wire and Darboux three-frame in case of curved film (Carro, 2016)), the total energy in the local reference frame can be rearranged as (Gaididei et al., 2014; Sheka et al., 2015a, 2020):

$$E = E_0 + \underbrace{E_A}_{\text{effective anisotropy}} + \underbrace{E_{mD}}_{\text{mesoscale DMI}} + \underbrace{E_{MS}}_{\text{magneto-statics}}. \quad (1)$$

The first energy contribution E_0 absorbs contributions which do not depend explicitly on the curvilinear properties of the system. The second term, an effective anisotropy, E_A comprises the intrinsic magneto-crystalline anisotropy E^{an} , the shape anisotropy, and extrinsic anisotropy, governed by the curvilinear geometry. In general, the effective anisotropy is of biaxial type, $E_A = \int d\mathbf{r} \mathcal{K}_{\alpha\beta} m_\alpha m_\beta$. Here and below Greek indices α, β, γ numerate curvilinear coordinates and curvilinear components of magnetization, while the Greek index ν indicates the curvilinear coordinate along the wire ($\nu = 1$), or two curvilinear coordinates inside the curved film ($\nu = 1, 2$). There are two major sources of this extrinsic anisotropy. One of them is driven by exchange. In case of curved wires the anisotropy coefficients have a bilinear form with respect to the wire curvature κ and its torsion τ , namely $\mathcal{K}_{\alpha\beta} = A \mathcal{F}_{\alpha\gamma} \mathcal{F}_{\beta\gamma}$ with $\mathcal{F}_{\alpha\beta}$ being the Frenet-Serret tensor determined by κ and τ (Sheka et al., 2015a). In case of curved films, $\mathcal{K}_{\alpha\beta}$ have a bilinear form with respect to principle curvatures κ_1 and κ_2 of the surface, namely $[\mathcal{K}_{\alpha\beta}] = \text{Adiag}(\kappa_1^2; \kappa_2^2; \kappa_1^2 + \kappa_2^2)$ (Sheka et al., 2020). The intrinsic DMI is additional source of the geometry-induced anisotropy: $\mathcal{K}_{\alpha\beta}$ is linear with respect to κ and τ for curved wires (Volkov et al., 2018); it is linear with respect to κ_1 and κ_2 for curved films (Kravchuk et al., 2018; Yershov et al., 2019).

The next term, the mesoscale DMI, $E_{mD} = \int d\mathbf{r} \mathcal{D}_{\alpha\beta\nu} \mathcal{L}_{\alpha\beta}^{(\nu)}$ is determined by the curvilinear-geometry analog of Lifshitz invariants $\mathcal{L}_{\alpha\beta}^{(\nu)} = m_\alpha \delta_\nu m_\beta - m_\beta \delta_\nu m_\alpha$ with $\delta_\nu \equiv \partial_s$ being the derivative with respect to the arc length s in case of curved wires (Volkov et al., 2018) and δ_ν being tangential derivatives with respect to the surface in case of curved films (Sheka et al., 2020). The mesoscale DMI adsorbs two different types of chiral interaction, which act at different lengthscales. While intrinsic DMI constants are determined by material parameters, extrinsic DMI constants essentially depend on local geometrical properties being linear with respect to curvatures. In particular, extrinsic DMI constants $\mathcal{D}_{\alpha\beta 1} = A \mathcal{F}_{\alpha\beta}$ for wires and $\mathcal{D}_{\alpha 3 \alpha} = 2A \kappa_\alpha$ for films (Sheka et al., 2020). The symmetry and amplitude of the resulting DMI are determined by both material and geometrical properties offering possibilities to tune both magnitude and directions of the mesoscale DMI by geometrical manipulations (Volkov et al., 2018).

Following the curvilinear formalism, the nonlocal magnetostatic interaction E_{ms} is restructured by involving three fictitious mathematical constructions in the description which are locally sensitive to the curved geometry (Sheka et al., 2020): A surface charge σ is determined by the normal component of magnetization. A tangential charge $\rho = -\delta_\nu m_\nu$ is determined by its tangential components (Sheka, 2021). The most intriguing term is the geometrical charge g , which represents the coupling between the magnetization texture and the geometrical curvature: $g = \kappa m_2$ in case of curved wires (Sheka, 2021) and $g = m; 210B; m_3$ in case of curved films (Sheka et al., 2020) with $m; 210B; m_3 = \kappa_1 + \kappa_2$ being the mean curvature. Usage of these three charges allows to restructure the magnetostatic interaction adapted to the curved geometry

$$E_{MS} = \underbrace{E_{\sigma-\sigma} + E_{\rho-\rho} + E_{\sigma-\rho}}_{E_{MS}^{\text{shape}}} + \underbrace{E_{g-\sigma} + E_{g-g} + E_{g-\rho}}_{E_{MS}^{\text{curv}}}, \quad (2)$$

where each term E_{a-b} describes the pair interaction between two charges of type 'a' and 'b', an explicit form (see in reference (Sheka et al., 2020)). While terms included in E_{MS}^{shape} do not depend explicitly on the curvature they fill the shape of the sample. The magnetostatic term E_{MS}^{curv} contains contributions, specific only to curved samples with a non-zero geometrical charges.

Curvature-induced Effects

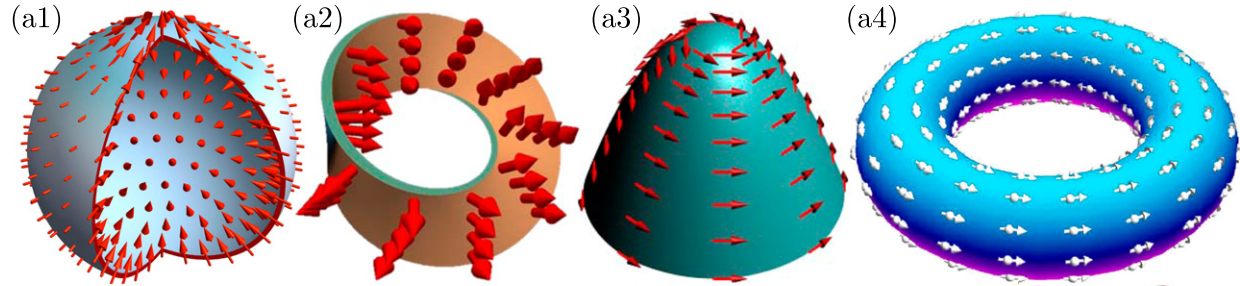
The curved geometry introduces emergent interactions, which are a prerequisite for diversity of curvature-induced effects in conventional magnetic materials. These effects can be classified using local and global properties of magnetic texture.

Topological patterning

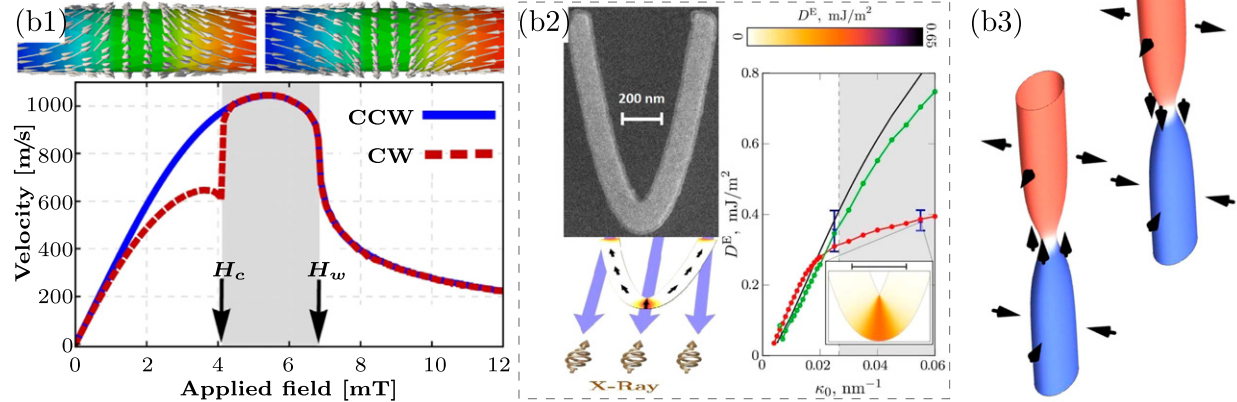
Topological magnetization patterning is a formation of topologically protected magnetization textures in topologically non-trivial curved geometries, supported by the interplay between magnetic subsystem and geometrical aspects of the underlying substrate (Sheka, 2021). A paradigmatic example is provided by a nanotube, which can support nontrivial textures, including transverse and vortex domain walls (Landeros and Núñez, 2010; López-López et al., 2012; Hertel, 2016) Néel, Bloch and cross-tie domain walls (Stano and Fruchart, 2018), Bloch-point domain walls (Da Col et al., 2014), in-surface and vortex states in straight cylindrical nanomagnets (Escrig et al., 2007) and analogous states in bent nanotubes (Mancilla-Almonacid et al., 2020). Most of these textures are topologically protected namely due to the topological properties of a nanotube, being object lessons of topological patterning.

Spherical shells correspond to a core-shell nanoparticles. The geometry of a spherical shell prohibits existence of a homogeneous magnetization texture, which would be preferable due to the exchange interaction even in the case of small spheres (Sloika et al., 2017). Instead, the texture with two topological defects (magnetic vortices) is realized in the case of the in-surface anisotropy: 3D onion state with the in-surface meridional direction of the magnetization in thin shells (Kravchuk et al., 2012), while a whirligig state with the in-surface magnetization oriented along parallels is typical for thick shells (Sloika et al., 2017). In the case of perpendicularly magnetized spherical shells (normal anisotropy), the hedgehog magnetic texture becomes preferable

(a) Topological patterning



(b) Geometrical magnetochiral effects



(c) Manipulation of topologically protected state by mesoscale DMI

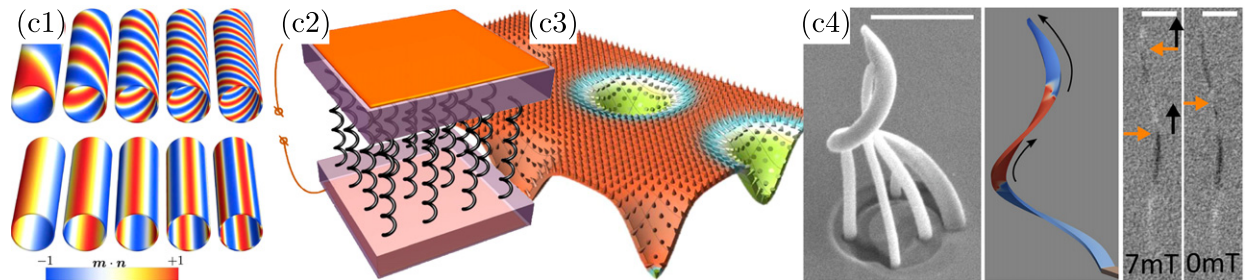


Fig. 1 Curvature-induced effects. (a) Topological patterning: (a1) skyrmion states in spherical nanoshells with easy-normal anisotropy, see Kravchuk *et al.* (2016) (Kravchuk, V.P., Röblier, U.K., Volkov, O.M., *et al.*, Physical Review B 94, 144402. <http://link.aps.org/doi/10.1103/PhysRevB.94.144402>); (a2) transversal domain wall in a Möbius ring, adapted with permission from (Pylypovskiy *et al.*, 2015) (Pylypovskiy, O.V., Kravchuk, V.P., Sheka, D.D., *et al.*, 2015. Coupling of chiralities in spin and physical spaces: The Möbius Ring as a case study. Physical Review Letters 114, 197204), © 2015 Authors, licensed under a Creative Commons Attribution 3.0 License; (a3) vortex pattern in paraboloid, reprinted from (Vilas-Boas *et al.*, 2015) (Vilas-Boas, P.S., Elias, R.G., Altir, D., Fonseca, J.M., Carvalho-Santos, V.L., 2015. Topological magnetic solitons on a paraboloidal shell. Physics Letters A 379, 47), © 2015, with permission from Elsevier; (a4) poloidal vortex in a toroidal nanoshell, adapted from (Teixeira *et al.*, 2019) (Teixeira, A.W., Castillo-Sepúlveda, S., Vojkovic, S., *et al.*, 2019. Analysis on the stability of in-surface magnetic configurations in toroidal nanoshells. Journal of Magnetism and Magnetic Materials 478, 253), © 2019, with permission from Elsevier. (b) Geometrical magnetochiral effects: (b1) Chiral break down of domain walls in a nanotube, unfavorable clockwise wall changes its chirality during the motion, adapted from (Otálora *et al.*, 2012) (Otálora, J.A., López-López, J.A., Vargas, P., Landeros, P., 2012. Chirality switching and propagation control of a vortex domain wall in ferromagnetic nanotubes. Applied Physics Letters 100, 072407), with the permission of AIP Publishing; (b2) Experimental observation of emergent DMI in parabolic nanostripes, reprinted figure with permission from (Volkov *et al.*, 2019a) (Volkov, O. M., Kákay, A., Kronast, F., *et al.*, 2019a. Experimental observation of exchange-driven chiral effects in curvilinear magnetism. Physical Review Letters 123, 077201), © 2019 by the American Physical Society; (b3) Selection of the domain wall handedness in a generalized cylinder, adapted with permission from (Sheka *et al.*, 2020) (Sheka, D.D., Pylypovskiy, O.V., Landeros, P., *et al.*, 2020. Nonlocal chiral symmetry breaking in curvilinear magnetic shells. Communications Physics 3, 128), © 2020 Authors, licensed under a Creative Commons Attribution 4.0 International License. (c) Manipulation of topologically protected state by mesoscale DMI: (c1) Inclined domain walls in nanotubes are realized due to the interplay between two types of DMI, adapted with permission from (Yershov *et al.*, 2020) (Yershov, K.V., Kravchuk, V.P., Sheka, D.D., Röblier, U.K., 2020. Curvature effects on phase transitions in chiral magnets. SciPost Physics 9, 43), © 2020 Authors, licensed under a Creative Commons Attribution 4.0 International License; (c2) Concept of artificial magnetoelectric materials, reproduced with permission from (Volkov *et al.*, 2019b) (Volkov, O.M., Röblier, U.K., Fassbender, J., Makarov, D., 2019b. Concept of artificial magnetoelectric materials via geometrically controlling curvilinear helimagnets. Journal of Physics D: Applied Physics © 2019 IOP Publishing; (c3) Reconfigurable skyrmion lattice, reproduced with permission from (Kravchuk *et al.*, 2018) (Kravchuk, V.P., Sheka, D.D., Kákay, A., *et al.*, 2018. Multiplet of skyrmion states on a curvilinear defect: Reconfigurable skyrmion lattices. Physical Review Letters 120, 067201), © 2018 American Physical Society; (c4) Experimental observation of the automation of domain wall in helical interconnector, reproduced with permission from (Skoric *et al.*, 2022) (Skoric, L., Donnelly, C., Hierro-Rodríguez, A., *et al.*, Domain wall automation in three-dimensional magnetic helical interconnectors. ACS Nano 16, 8860), © 2022 Authors, licensed under a Creative Commons Attribution 4.0 International License (CC BY 4.0).

(Kravchuk *et al.*, 2016). Besides, the curvature-induced exchange-driven DMI is responsible for the formation of the skyrmion state (Kravchuk *et al.* 2016), see Fig. 1 (a1).

The topology of circular nanorings support vortex states (Guimarães, 2017), nonorientable Möbius rings can host vortices, topologically protected longitudinal and transversal domain walls (Pylypovskyi *et al.*, 2015), see Fig. 1 (a2). Toroidal shells can support single-domain states, toroidal, and poloidal (Fig. 1 (a4)) vortex states (Vojkovic *et al.*, 2016; Teixeira *et al.* 2019), vortex-antivortex pairs (Vojkovic *et al.*, 2017). Under the action of magnetic field magnetization reversal modes can be accompanied by the appearance of magnetic hopfions (Castillo-Sepúlveda *et al.*, 2021). Hyperboloid and paraboloid shells can support a specific shape of vortex (Fig. 1 (a3)), skyrmion and skyrmionium states (Carvalho-Santos *et al.*, 2015; Vilas-Boas *et al.*, 2015).

Geometrical magnetochiral effects

The spatial inversion symmetry in curved magnets is lower or broken than in straight and flats samples. That is the main reason of emergent chiral interactions in curvilinear magnetism. Geometrical magnetochiral effects represent magnetization textures with their chirality governed by the curved geometry.

Pattern-induced chiral symmetry breaking

A pattern-induced chiral symmetry breaking (Streubel *et al.*, 2016) means a violation of the chiral symmetry of magnetization texture on the background of a chiral-degenerated static magnetization texture. Such breaking occurs dynamically. One of the well-studied example corresponds to tubular nanoshells: while the static vortex state tube (Zimmermann *et al.*, 2018) and vortex domain walls (Landeros and Núñez, 2010) are degenerate with respect to their chirality, these textures can serve as springboard for magnon chiral effects. It is possible to excite spin waves, propagating along the tube axis: the pair interaction between different types of magnetostatic charges, see Eq. 2, causes the coupling between the normal and tangential components of the dynamic magnetization (Sheka *et al.*, 2020). Finally, this coupling becomes a source of chirality dependent magnon splitting on the background of the vortex state in a nanotube (Otálora *et al.*, 2016; Otálora *et al.*, 2017). Asymmetric spin-wave dispersion was observed in magnetic nanotubes with hexagonal cross-section using time resolved scanning transmission X-ray microscopy (Körber *et al.*, 2020). Another chiral pattern, the vortex domain wall (Landeros and Núñez, 2010), can support a chiral symmetry breaking (Otálora *et al.*, 2012; Yan *et al.*, 2012; Otálora *et al.*, 2013; Hertel, 2013), see Fig. 1 (b1). Besides, it can trigger a Cherenkov-type spin-wave radiation (Yan *et al.*, 2011, 2013) suppressing the Walker breakdown (Yan *et al.*, 2010).

Geometry-induced chiral symmetry breaking

A geometry-induced chiral symmetry breaking (Streubel *et al.*, 2016) corresponds to the break of a chiral degeneracy of the magnetic interaction due to the interplay between the geometrical properties of the substrate such as local curvatures, and the magnetochirality (Hertel, 2013) of the texture. Chiral interactions are able to select handedness for achiral textures known (Chen and Schmid, 2015). In flat parabolic stripes the curvature-induced DMI provides the phase selection of domain walls (Yershov *et al.*, 2015a; Volkov *et al.*, 2019a), see Fig. 1 (b2). In curved shells, the emergent DMI is responsible for the curvature-induced selection of the winding number of a meron in hyperbolic and parabolic nanoshells (Elas *et al.*, 2019). In helicoid ribbons, the emergent DMI selects the preferable magnetization handedness of the ground state (Gaididei *et al.*, 2017). Namely, the emergent DMI is the reason of specific remanent vortex-antivortex states in hollow toroidal nanomagnets (Vojkovic *et al.*, 2017). Due to the geometry-induced chiral symmetry breaking the magnetochirality of domain walls in Möbius rings is determined by the geometrical chirality of the ring (Pylypovskyi *et al.*, 2015). The emergent DMI in helix wires provides the charge dependent domain wall handedness (Yershov *et al.*, 2016). Representative consequences of the coupling between the geometrical helix chirality and the magnetochirality is the nonreciprocity of the spin-wave spectrum (Sheka *et al.*, 2015b), the chirality sensitive domain wall mobility (Pylypovskyi *et al.*, 2016) and a negative mobility of the spin-torque driven domain wall (Yershov *et al.*, 2016).

Nonlocal magnetochiral symmetry break

Nonlocal magnetochiral effect (Sheka *et al.*, 2020) introduces handedness in an intrinsically achiral material and enables the design of magnetoelectric and ferrotoroidic responses. It originates from the pair interaction of tangential, surface and geometrical charges in the magnetostatic interaction, see Eq. 2, being essentially nonlocal. This chiral symmetry break provides the possibility to stabilize the preferred handedness of a nonlocal magnetic texture, for example, the domain wall in the intrinsically not chiral magnets even in statics (Fig. 1 (b3)), which is technologically relevant for current-driven domain wall motion in racetrack memory and domain wall logic devices (Sheka *et al.*, 2020).

Topological chiral coupling

Topological chiral coupling is the interconnection between the geometrical chirality of the substrate, magnetochirality of the texture and its topological charge, caused by the geometry-induced chiral symmetry breaking for topologically non-trivial textures. In particular, the emergent DMI in helix wires provides the charge dependent domain wall handedness (Yershov *et al.*, 2016). The topological chiral coupling selects the magnetochirality of the Bloch domain walls in twisted stripes depending on its geometrical chirality and the domain wall charge (Sheka *et al.*, 2022b). Topological chiral coupling occurs also for another topological texture, the magnetic vortex on a spherical shell, where the magnetochirality is reflected in the coupling between the directions of in-surface magnetization curling and out-of-plane magnetization component, circulation and polarity, respectively (Kravchuk *et al.*, 2012). Geometrical asymmetry of disks caused by the surface roughness, is known to be a reason of the coupling between the vortex polarity and its circulation (Curcic *et al.*, 2008; Vansteenkiste

et al., 2009). The polarity-circulation coupling was also investigated for merons in parabolic and hyperbolic shells (Elas *et al.*, 2019). The selection of the vortex magnetochirality in spherical caps is also caused by the polarity-circulation coupling (Sheka *et al.*, 2022b).

Manipulation of topologically protected state by mesoscale DMI

Geometrical manipulations of materials using combinations of emergent geometry-governed DMI and intrinsic DMI give rise to mesoscale DMI providing ample opportunities for geometrical manipulations of material responses (Volkov *et al.*, 2018).

Pinning of excitations by emergent DMI

Geometry-governed exchange-driven DMI in curved achiral magnets can influence different excitations in curved magnets providing ample ways for manipulations. The emergent DMI proportional to the curvature gradient appears at the local bends of nanowires and films, acting as a driving force. By bending the flat wire one can bind linear excitations, i.e. spin waves: eigenfrequency of a truly local magnon mode is determined by the curvature of the wire (Gaididei *et al.*, 2018). One can also manipulate by nonlinear excitations, such as domain walls. In particular, the phase-selected pinning of transversal domain walls take place at the maximum curvature of local bend of the parabolic wire (Yershov *et al.*, 2015a). By measuring the depinning field of domain walls, the effective exchange-driven DMI constant is quantified experimentally (Volkov *et al.*, 2019a), see Fig. 1 (b2). Two-dimensional topological texture, magnetic skyrmion can also be pinned in similar way: the driving force in a curved film is determined by the gradient of the mean curvature (Korniienko *et al.*, 2020), leading to the pinning of the skyrmion on the bump (Kravchuk *et al.*, 2018; Korniienko *et al.*, 2020).

Geometry-induced drift by emergent DMI

Internal-to-the-system geometry-governed drift of transversal domain walls in curved nanostripes is driven by a gradient of the curvature. Such automotion in Euler spiral nanostripes acquire remarkably high velocities of up to 100 m/s and do not exhibit any Walker-type speed limit (Yershov *et al.*, 2018). The geometry-driven automotion of domain walls in helical interconnectors is experimentally detected (Skoric *et al.*, 2022), see Fig. 1 (c4). In similar way the curvature gradients causes the drift of skyrmions. The strength of the curvature-induced driving force essentially depends on the skyrmion type (Néel or Bloch type), while the trajectory of motion is determined by the type of the magnetic ordering (ferro- or antiferromagnetic) (Yershov *et al.*, 2022).

New topologically stable states engineered by mesoscale DMI

The magnetic phase-diagram of curvilinear magnets becomes much richer as compared to flat specimens. This is typically caused by the mesoscale DMI through the interplay between intrinsic and extrinsic chiral interactions. In particular, such an interplay favors skyrmions with different helicity numbers for the spherical nanoshell (Kravchuk *et al.*, 2016); it increases (decreases) the stability of skyrmions in dome (antidome) structures (Carvalho-Santos *et al.*, 2020), cylindrical nanostripes and nanotubes (Kechrakos *et al.*, 2020). The mesoscale DMI results in a new type of inclined domain walls in nanotubes (Yershov *et al.* 2020; Liu *et al.*, 2020), see Fig. 1 (c1). A localized curvilinear defect can favor the multiplet of skyrmion states with a perspective to be utilized to encode and switch a bit of information (Kravchuk *et al.*, 2018). Such a defect can pin a skyrmion and the curvature-induced drift of the skyrmion is typically driven by the gradient of the local surface mean curvature (Korniienko *et al.*, 2020). The periodically arranged lattice of the curvilinear defects can generate a skyrmion lattice as a ground state (Kravchuk *et al.*, 2018), see Fig. 1 (c3).

Concept of artificial magnetoelectric materials

An efficient way for geometrical manipulations of material responses is offered by artificial magnetoelectric materials (Volkov *et al.*, 2018). The concept is elaborated for curvilinear helimagnets sandwiched between two piezoelectric layers (Volkov *et al.*, 2019b), see Fig. 1 (c2). By applying the electric field to the piezoelectric material, one can induce tiny changes in geometrical deformations of the curvilinear helimagnet. This in turn leads to the reversible magnetic phase transition between two types of magnetic textures: homogeneous and periodic magnetic states (Volkov *et al.*, 2018). The phase transition is caused by the change of the mesoscale DMI constant through the critical value by modifying the geometrical parameters of the helimagnet. The concept of artificial magnetoelectric material relies on the converse magnetoelectric effect, which is defined as the change in the magnetic moment responding to the applied electric field. This is a significant enhancement of the converse magnetoelectric coefficient compared to the common magnetoelectric systems (Volkov *et al.*, 2019b).

Fabrication and Characterization

Methods of Fabrication

It is a peculiarity of curvilinear magnetic nano-architectures to keep a balance between low dimensionality of a nanomagnetism and the complex-shaped design to achieve new features of the curved geometry.

Electron beam lithography

Typically curvilinear flat architectures are fabricated using conventional techniques based on thin film deposition and lithographic methods. Electron beam lithography (EBL) is the most developed technique, which is widely used to fabricate planar curved nanowires (Thomas *et al.*, 2006; Westphalen *et al.*, 2008; Kim *et al.*, 2014), stripes (Lewis *et al.*, 2009; Volkov *et al.*, 2019a), and nanorings (Kläui *et al.*, 2003; Castano *et al.*, 2003).

Rolled-up nanotech

Strain engineering rolled-up nanotech is a 3D nanotechnology based on thin films (Schmidt and Eberl, 2001; Deneke *et al.*, 2009). It relies on differential strain in thin films allowing to fabricate cylindrical and helical thin-film structures (Streubel *et al.*, 2016). The rolled-up nanotech allows to develop novel materials, including a variety of rolled-up and wrinkled magnetic nanomembranes such as microhelix coil structures (Smith *et al.*, 2011), Swiss rolls (Balhorn *et al.*, 2010), magnetically capped cylinders (Streubel *et al.*, 2012a) and complex micro-origami structures (Gabler *et al.*, 2019).

Template-assisted strategies

Template-assisted strategies include self-assembly, combinations of 3D templates usage with electroless and atomic layer deposition, electroplating (Streubel *et al.*, 2016; Fernández-Pacheco *et al.*, 2017). This allows to fabricate core-shell nanowires (Ozel *et al.*, 2015), multilayered nanotubes (Zierold *et al.*, 2010). Synthesis of hollow magnetic nanoparticles include template-assisted strategies with hard and soft templates as well as sacrificial templates and template-free methods (He *et al.*, 2012). Typical hollow nanostructures are hollow spherical particles (Sayed *et al.*, 2018) (Fig. 2 (a)), nano-rings, nano-tubes (Jia *et al.*, 2008), core/shell nanoparticles (López-Ortega *et al.*, 2015). Interconnected nanowire networks have been achieved recently using electro-deposition into polycarbonate membranes (Burks *et al.*, 2020). Other template-assisted strategies exploit non-magnetic curvature templates using nanoporous templates (Vázquez, 2015), polymer templates (Seniutinas *et al.*, 2018), ion-induced surface patterning (Fassbender *et al.*, 2009), and nanosphere lithography (Albrecht *et al.*, 2005). Ion-induced surface nanopatterning allows formation of periodic surface patterns via nanoscale self-assembly (Fassbender *et al.*, 2009). This technique is used to achieve array of nanocones (Ball *et al.*, 2014) (Fig. 2 (d)) and ripples (Ou *et al.*, 2015). Nanosphere lithography (NSL) is a method of fabrication arrays of magnetic spherical nanoparticles (Albrecht *et al.*, 2005); (Colson *et al.*, 2013). The first step of NSL process includes preparation of the mask (a monolayer of nanoparticles) using one of the following methods: self-assembly at liquid-liquid interface (Hu *et al.*, 2012) or at air-liquid interface (Liu *et al.*, 2019), a drop casting (Micheletto *et al.*, 1995), spin coating (Chen *et al.*, 2013), dip coating (Núñez *et al.*, 2018). The second step is the deposition of the magnetic material through the mask. NSL allows to create isolated hemispherical and cylindrical caps as well as cap arrays, caps with different anisotropy orientation; such cap structures host vortices, skyrmions and more complex spin textures (Streubel *et al.*, 2016). NSL can also be used to nanoindentations, which can be covered by magnetic thin films (Makarov *et al.*, 2007), see Fig. 2 (e).

Glancing angle deposition

Glancing angle deposition (GLAD) is a method to fabricate nanostructured columnar architectures using common physical vapor deposition processes (Hawkeye *et al.*, 2014). By tilting the substrate during deposition allows to grow array of sculpted 3D objects such as helices, posts, and chevrons (Dick *et al.*, 2000). GLAD technique allows to fabricate freestanding 3D nanostructures such as 3D nanospirals with a wire diameter of 20 nm and outer spiral diameter of 115 nm (Phatak *et al.*, 2014), see Fig. 2 (c). A chiral nickel film consisting of an array of nanohelices 100 nm in length a helix pitch of 50 nm was reported in Eslami *et al.* (2014). Ultimately small nanohelices of dimensions reaching a length of 50 nm and helix pitch of 25 nm were achieved in Gibbs *et al.* (2014). Typically, this method is limited by helical and columnar geometries.

Two-photon lithography

Conventional photolithography generally relies on single-photon absorption in a photoresist (Pimpin and Srituravanich, 2012). Instead, two-photon lithography (TPL) uses a femtosecond laser pulse for two-photon polymerization of the photoresist in a controlled local region, which allows to fabricate 3D magnetic nanostructures (Hunt *et al.*, 2020). Fabrication of magnetic nanostructures with TPL include different metallization techniques such as electrochemical deposition, line of sight deposition (Hunt *et al.*, 2020), which allows to fabricate rapidly complex 3D nanostructures with examples of tetrapod individual structure and their array (Sahoo *et al.*, 2018; Williams *et al.*, 2018; Askey *et al.*, 2020), buckyball structure (Fig. 2 (h)) and trefoil-knots (Pip *et al.*, 2020).

Focused electron beam-induced deposition

The focused electron beam induced deposition (FEBID) is a method to fabricate complex-shaped 3D nano-architectures (Huth *et al.*, 2018; Winkler *et al.*, 2019; Plank *et al.*, 2019,2020), it enables to pattern complex 3D magnetic nanostructures at resolutions comparable to the characteristic magnetic length scales (Fernández-Pacheco *et al.*, 2020). In this method the focused electron beam is provided by a scanning electron microscope, the vertical lateral resolution down to 1 nm and lateral resolution to few nm can be achieved (van Dorp *et al.*, 2005). FEBID nanoprinting is used to fabricate complex 3D nanowires including nanospirals (Fernández-Pacheco *et al.*, 2013), nanobridges (Lau *et al.*, 2002), nanohelices (Phatak *et al.*, 2020), 3D magnetic helical interconnectors (Skoric *et al.*, 2022), double-helices (Sanz-Hernández *et al.*, 2020) (Fig. 2 (g)), artificial structures like tetrapods, tetrahedra (Fernández-Pacheco *et al.*, 2020), nanotrees (Fig. 2 (f)), nanocubes and their lattices (Keller *et al.*, 2018), and exotic 3D object with curved surfaces such as Möbius nanorings (Winkler *et al.*, 2019) (Fig. 2 (i)), also magnetic (Skoric *et al.*, 2020) and nanovolcanoes (Fernández-Pacheco *et al.*, 2020; Dobrovolskiy *et al.*, 2021) (Fig. 2 (j)).

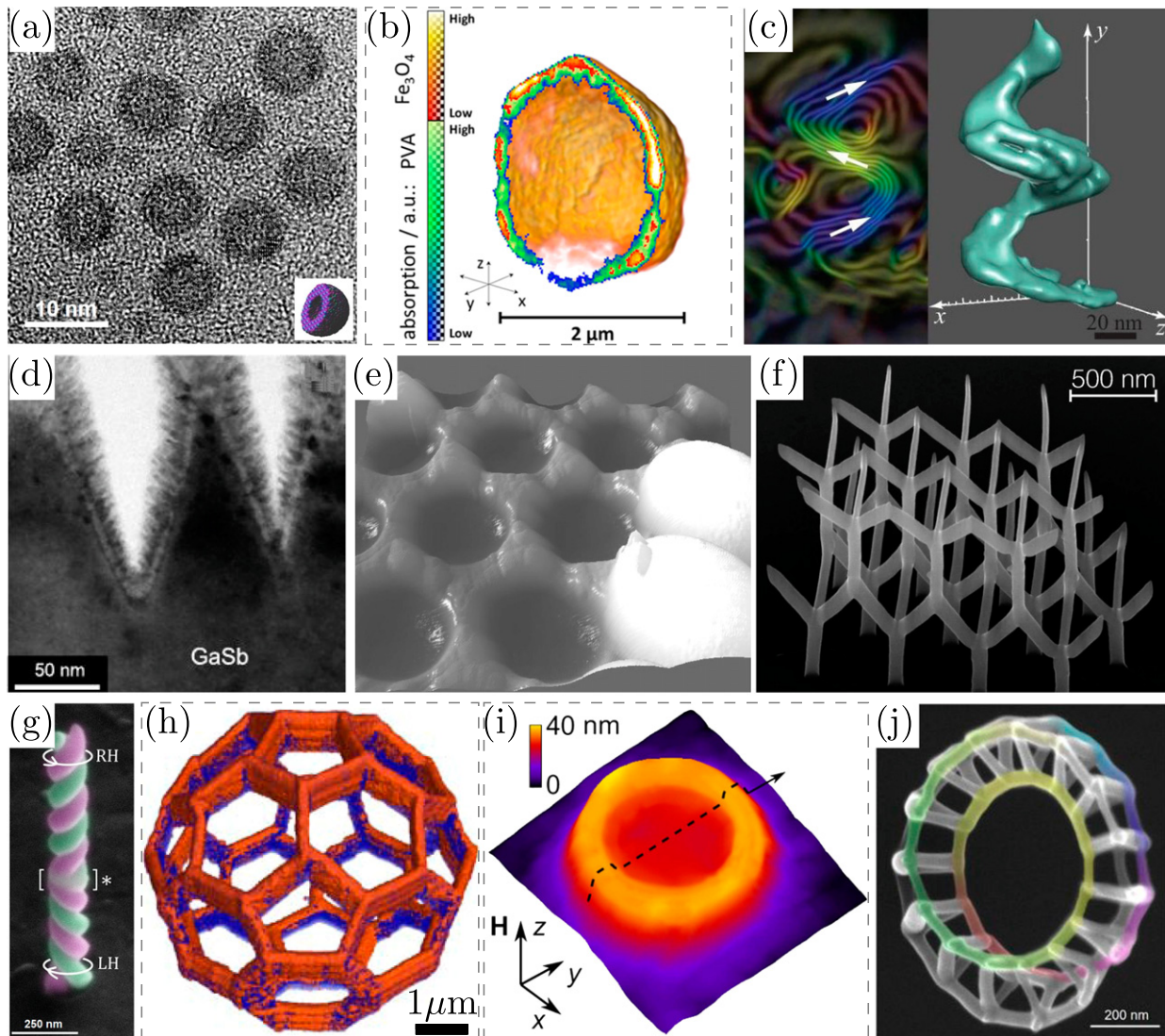


Fig. 2 Experimental realization of curvilinear nanomagnets. (a) TEM images of hollow γ -Fe₂O₃ spherical nanoparticles, adapted with permission from (Sayed *et al.*, 2018) (Sayed, F., Yaacoub, N., Labaye, Y., *et al.*, 2018. Surface effects in ultrathin iron oxide hollow nanoparticles: Exploring magnetic disorder at the nanoscale. The Journal of Physical Chemistry C 122, 7516), © 2018 American Chemical Society; (b) Soft X-ray laminography of PVA microsphere coated with Fe₃O₄ nanoagglomerates, adapted with permission from (Witte *et al.*, 2020) (Witte, K., Späth, A., Finizio, S., *et al.*, 2020. From 2D STXM to 3D imaging: Soft X-ray laminography of thin specimens. Nano Letters 20, 1305), © 2020 American Chemical Society; (c) Electron holography image of the magnetization texture in Co nanohelix produced using the GLAD technique, adapted with permission from (Phatak *et al.*, 2014) (Phatak, C., Liu, Y., Gulsoy, E.B., *et al.*, 2014. Visualization of the magnetic structure of sculpted three-dimensional cobalt nanospirals. Nano Letters 14, 759), © 2014 American Chemical Society; (d) TEM images of 3D template with GaSb nanocones coated with Co/Pd multilayer, adapted with permission from (Ball *et al.*, 2014) (Ball, D.K., Lenz, K., Fritzsche, M., *et al.*, Magnetic properties of granular CoCrPt:SiO₂ thin films deposited on GaSb nanocones. Nanotechnology 25, 085703), © 2014 IOP Publishing; (e) AFM images of spherical nanoindentations with perpendicular anisotropy, reprinted from (Makarov *et al.*, 2007) (Makarov, D., Baraban, L., Guhr, I.L., *et al.*, 2007. Arrays of magnetic nanoindentations with perpendicular anisotropy. Applied Physics Letters 90, 093117), with the permission of AIP Publishing; (f) SEM images of nano-tree array fabricated by FEBID with the precursor HCo₃Fe(CO)₁₂, reproduced with permission from (Keller *et al.*, 2018) (Keller, L., Mamoori, M.K.I.A., Pieper, J., *et al.*, 2018. Direct-write of free-form building blocks for artificial magnetic 3D lattices. Scientific Reports 8, 6160), © 2018 Authors, licensed under a Creative Commons Attribution 4.0 International License; (g) SEM image of the Co nanostructure consisting of two double-helices of opposite chirality joined at the tendril perversion marked with*, fabricated by FEBID, adapted with permission from (Sanz-Hernández *et al.*, 2020) (Sanz-Hernández, D., Hierro-Rodríguez, A., Donnelly, C., *et al.*, 2020. Artificial double-helix for geometrical control of magnetic chirality. ACS Nano 14, 8084), © 2020 Authors, licensed under a Creative Commons Attribution 4.0 International License (CC BY 4.0); (h) Tomogram of the Co-coated artificial buckyball, adapted with permission from (Donnelly *et al.*, 2015) (Donnelly, C., Guizar-Sicairos, M., Scagnoli, V., *et al.*, 2015. Element-specific X-ray phase tomography of 3D structures at the nanoscale. Physical Review Letters 114, 115501), © 2015 by the American Physical Society; (i) AFM image of Co₃Fe nanovolcano fabricated by FEBID, reprinted from (Dobrovolskiy *et al.*, 2021) (Dobrovolskiy, O.V., Vovk, N.R., Bondarenko, A.V., *et al.*, 2021. Spin-wave eigenmodes in direct-write 3D nanovolcanoes. Applied Physics Letters 118, 132405) with permission of AIP Publishing; (j) SEM image of Möbius strip with triangular cross section and individual wire dimensions around 25 nm fabricated by FEBID, reprinted from (Winkler *et al.*, 2019) (Winkler, R., Fowlkes, J.D., Rack, P.D., Plank, H., 2019. 3D nanoprinting via focused electron beams. Journal of Applied Physics 125, 210901) with permission of AIP Publishing.

Methods of Characterization

Conventional characterization techniques of magnetic structures at nanoscale are suitable for planar textures. Curved architectures requires advanced 3D techniques since 3D-shaped nanoobjects can hide substantial parts of their structure for conventional top-view imaging. Besides, 3D structural and magnetic properties of 3D nanoobjects are typically caused by complex vector properties of magnetization field defined on the curved substrate (Streubel *et al.*, 2016; Fernández-Pacheco *et al.*, 2017; Fischer *et al.*, 2020; Streubel *et al.*, 2021; Makarov *et al.*, 2022).

Magneto-optical microscopies

Magneto-optical microscopies are the most widely used techniques in 2D magnetism, providing observation of complex inhomogeneous textures (Hubert and Schäfer, 2009). Based on the magneto-optical Kerr effect (MOKE) or Faraday effect, magneto-optical microscopy and magnetometry are the most prominent techniques to visualize magnetization fields within magnetic materials (McCord, 2015). Deep nanoscale magnetic imaging provides a possibility to visualize ultrafast magnetization dynamics in a nanoscale 3D tetrapod structure (Sahoo *et al.*, 2018), 3D frustrated magnetic nanowire lattice (May *et al.*, 2019). A dark-field magneto-optical imaging (McCord, 2015) allows to detect independently different areas of 3D nanosystem (Sanz-Hernández *et al.*, 2017). Combination with magneto-transport measurements allows to determine the magnetic hysteresis loops for nano-tree and nano-cube structures (Mamoori *et al.*, 2018) and to detect the gigantic Hall effect in a spin hedgehog crystal (Kanazawa *et al.*, 2020).

X-ray characterization

X-ray-based microscopies utilize X-ray magnetic linear dichroism (XMLD) or magnetic circular dichroism (XMCD) effects as magnetic contrast mechanisms (Kuch *et al.*, 2015). Currently the most powerful techniques for imaging 3D magnetic nanotextures are advanced X-ray spectromicroscopies such as X-ray photoemission electron microscopy (XPEEM), magnetic transmission soft X-ray microscopy (MTXM), scanning transmission X-ray microscopy (STXM), X-ray holography, laminography and ptychography, X-ray vector field tomography (Streubel *et al.*, 2016; Fernández-Pacheco *et al.*, 2017; Fischer *et al.*, 2020; Streubel *et al.*, 2021). Different domain patterns in individual hemispherical Permalloy caps were visualized by XPEEM (Streubel *et al.*, 2012b). XMCD images allows to visualize complex 3D magnetization texture of two double-helices of opposite chirality (Sanz-Hernández *et al.*, 2020). Resonant ptychographic tomography, which combines quantitative hard X-ray phase imaging and resonant elastic scattering allows to achieve 3D characterization of a cobalt-coated artificial buckyball (Donnelly *et al.*, 2015) (Fig. 2 (h)). Soft-X-ray tomography is used for visualization and reconstruction of magnetic domain structures in a 3D curved magnetic tubular and rolled-up structures (Streubel *et al.*, 2015), complex 3D topological texture like magnetic bubbles and their lattices (Turnbull *et al.*, 2020). Soft X-ray ptychography is a powerful tool for imaging of magnetic domains and skyrmions at length scales below 100 nm (Bykova *et al.*, 2018). Spherical core-shell nanoparticles are well suited to soft X-ray laminography (Witte *et al.*, 2020) (Fig. 2 (b)), 3D magnetic structure in the vicinity of Bloch points (magnetic singularities) can be observed using hard-X-ray vector nanotomography (Donnelly *et al.*, 2017). Time-resolved magnetic laminography allows to image fast dynamic response of 3D magnetization in nanodisks (Donnelly *et al.*, 2020).

Advanced electron microscopies

High-resolution characterization of curved 3D magnets is achieved by transmission electron microscopy (TEM). Today TEM include a number of magnetic characterization techniques such as Lorentz transmission electron microscopy (Graef, 2001), scanning transmission electron microscopy (STEM) (Pennycook and Nellist, 2011), electron holography (Dunin-Borkowski *et al.*, 2019), differential phase contrast imaging (Lopatin *et al.*, 2016), vector field electron tomography (Phatak *et al.*, 2008). Direct visualization of complex magnetic texture in 3D Co nanospirals magnetic structure at a nanometer spatial resolution was realized by Lorenz TEM (Phatak *et al.*, 2014), see Fig. 2 (c). Skyrmion tubes were observed by magnetic force microscopy (Milde *et al.*, 2013). Electron holography allows observation of magnetization distribution inside chiral magnetic bobbars (Zheng *et al.*, 2018), single-domain/vortex state in nanocube (Gatel *et al.*, 2015). Using vector field electron tomography the 3D magnetization texture was studied for 3D nanowires (Phatak and Gürsoy, 2015; Wolf *et al.*, 2019), curved nanohelices (Phatak *et al.*, 2020). Magnetization texture of tetrapod structures are observed by spin-polarized scanning electron microscopy (spin-SEM) (Williams *et al.*, 2018).

Other techniques

Neutron microscopy is traditional way for studying magnetic materials in large volumes (Mühlbauer *et al.*, 2019). Talbot-Lau neutron tomography is a method suitable for 3D imaging of nanomagnets (Manke *et al.*, 2010). Among other methods for characterization curved magnets one has to mention Brillouin light scattering (BLS) (Demokritov *et al.*, 2001; Gubbiotti, 2019) (Fig. 3 (f)) and nitrogen-vacancy (NV) magnetometry (Gross *et al.*, 2017; Hedrich *et al.*, 2021), scanning SQUID magnetometry of nanowires (Martnez-Pérez *et al.*, 2018), nanotubes (Vasyukov *et al.*, 2018), nanocubes (Anahory *et al.*, 2020), Janus particles (Baraban *et al.*, 2012), and reconfigurable magnetic force microscopy (Kazakova *et al.*, 2019).

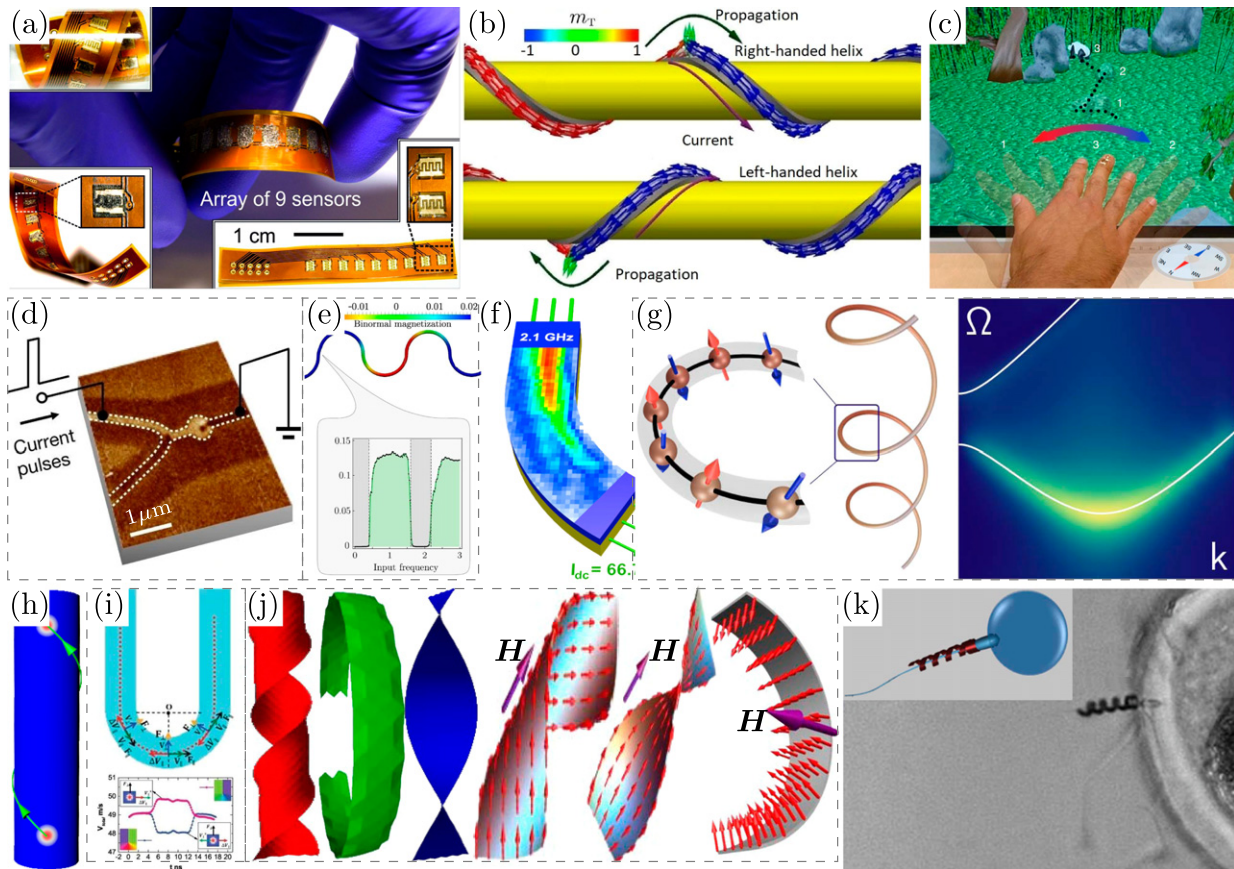


Fig. 3 Applied curvilinear magnetism. Shapeable magnetoelectronics: (a) flexible and printable high performance GMR sensors, adapted with permission from (Karnaushenko *et al.*, 2015) (Karnaushenko, D., Makarov, D., Stöber, M., *et al.*, 2015. High-performance magnetic sensors for printable and flexible electronics. *Advanced Materials* 27, 880), © 2014 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (c) geomagnetic interaction with a virtual reality environment, reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, Nature Electronics (Cañón Bermúdez *et al.*, 2018) (Cañón Bermúdez, G.S., Fuchs, H., Bischoff, L., Fassbender, J., Makarov, D., *et al.*, Electronic-skin compasses for geomagnetic field-driven artificial magnetoreception and interactive electronics. *Nature Electronics* 1, 589, © 2022). Curvilinear spintronics: (b) chiral symmetry breaking in the domain wall mobility in helix wires, adapted with permission from (Pylypovskiy *et al.*, 2016) (Pylypovskiy, O.V., Sheka, D.D., Kravchuk, V.P., *et al.*, 2016. Rashba torque driven domain wall motion in magnetic helices. *Scientific Reports* 6, 23316), © 2016 Authors, licensed under a Creative Commons Attribution 4.0 International License; (d) MFM images of the magnetic configuration of the Y-shaped domain wall racetrack, reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, Nature, (Luo *et al.*, 2020) (Luo, Z., Hrabec, A., Dao, T.P., *et al.*, 2020. Current-driven magnetic domain-wall logic. *Nature* 579, 214), © 2020. Curvilinear magnonics: (e) concept of curvature-induced magnonic crystal, adapted with permission from (Kornienko *et al.*, 2019) (Kornienko, A., Kravchuk, V., Pylypovskiy, O., *et al.*, 2019. Curvature induced magnonic crystal in nanowires. *SciPost Physics* 7, 35), © 2019 Authors, licensed under a Creative Commons Attribution 4.0 International License; (f) Brillouin light scattering detection of spin waves in curved micro-waveguide, reproduced from (Vogt *et al.*, 2012) (Vogt, K., Schultheiss, H., Jain, S., *et al.*, 2012. Spin waves turning a corner. *Applied Physics Letters* 101, 042410), with the permission of AIP Publishing; (g) geometrically tunable spin-wave spectrum in the antiferromagnetic helix, reprinted with permission from (Pylypovskiy *et al.*, 2020) (Pylypovskiy, O.V., Kononenko, D.Y., Yershov, K.V., *et al.*, 2020. Curvilinear one-dimensional antiferromagnets. *Nano Letters* 20, 8157), © 2020 American Chemical Society. Curvilinear skyrmionics: (h) current-induced skyrmion propagation in a nanotube, adapted with permission from (Wang *et al.*, 2019) (Wang, X., Wang, X.S., Wang, C., *et al.*, 2019. Current-induced skyrmion motion on magnetic nanotubes. *Journal of Physics D: Applied Physics* 52, 225001), © 2019 IOP Publishing; (i) current-driven skyrmion movement in a curved nanotrack, adapted with permission from (Cai and Liu, 2021) (Cai, N., Liu, Y., 2021. *Journal of Physics D: Applied Physics* 54, 125001), © 2015 IOP Publishing. Magnetic soft robotics: (j) field control of the shape of flexible ferromagnetic ribbons with DMI, adapted with permission from (Yershov *et al.*, 2019) (Yershov, K.V., Kravchuk, V.P., Sheka, D.D., van den Brink, J., Gaididei, Y., 2019. Spontaneous deformation of flexible ferromagnetic ribbons induced by Dzyaloshinskii-Moriya interaction. *Physical Review B* 100, 140407(R)), © 2019 <https://doi.org/10.1103/PhysRevB.100.140407> by the American Physical Society; (k) sperm-carrying micromotors, adapted with permission from (Medina-Sánchez *et al.*, 2016) (Medina-Sánchez, M., Schwarz, L., Meyer, A. K., Hebenstreit, F., Schmidt, O.G., 2016. Cellular cargo delivery: Toward assisted fertilization by sperm-carrying micromotors. *Nano Letters* 16, 555), © 2016.

Future Directions

Thriving fabrication and characterization techniques of curvilinear magnets provide wide testing area for fundamental research of novel effects induced by geometrically curved materials. Besides, these techniques allow studying fundamental problems of curvilinear magnetism, exploitation of 3D nano-architectures in novel devices with prospective applications.

Fundamental Physics viewpoint

Curvilinear magnetism provides a prospective route to realize topological textures by geometrical manipulations. The future challenge is to study dynamics of topological magnetic solitons in curved magnets. Controllable switching of chirality of magnetic vortex (Yershov *et al.*, 2015b) and chirality-dependent switching of the vortex core (Sloika *et al.*, 2014) in hemispherical caps structures have elucidated the role of curvature in switching phenomena. Further progress in curvilinear-geometry assisted switching phenomena and the current-driven dynamics of topologically protected states is important for potential applications in curvilinear spintronics (Section "Curvilinear spintronics") and curvilinear skyrmionics (Section "Curvilinear magnonics").

Curvilinear antiferromagnetism offers essential fundamental and application potential (Makarov *et al.*, 2022). To the moment the general micromagnetic framework of curvilinear magnetism is constructed for ferromagnets only (Sheka *et al.*, 2020). The peculiarity of antiferromagnets is the phenomenon of frustration (Diep, 2013). Geometrically curved antiferromagnets of non-trivial topology support new topologically nontrivial states: in particular, the close loop geometry can favor kinklike solitons and Möbius states (Castillo-Sepúlveda *et al.*, 2017). Very recently a concept of curvilinear antiferromagnet was introduced for one dimensional spin chains: the geometry-governed exchange-driven Dzyaloshinskii–Moriya interaction is geometrically tunable and is responsible for the helimagnetic phase transition (Pylypovskiy *et al.*, 2020). An extension of theory beyond the σ -model allows to describe curvilinear 1D antiferromagnets and determine conditions when they possess the geometry-driven weak ferromagnetism: in contrast to ferromagnets, antiferromagnets exhibit the geometry-driven modification of the magnetic responses stemming also from the anisotropy interaction (Pylypovskiy *et al.*, 2021). Topological arguments about similarity between order parameters in antiferromagnets and liquid crystals (Napoli *et al.*, 2021) suggest that curvilinear antiferromagnets can support topological textures similar to liquid crystals, in particular, ground state disclinations (Vitelli and Nelson, 2006) and boojums (Kleman and Lavrentovich, 2006). Experimental studies of curved antiferromagnets is available within molecular magnetism (Blundell, 2007; Schnack, 2019). Different curved antiferromagnets are synthesized and characterized as zigzag-shaped nanowires (Folven *et al.*, 2011), antiferromagnetic wheels (Baker *et al.*, 2012; Coletta *et al.*, 2021) Möbius rings (Cador *et al.*, 2004; Guidi *et al.*, 2015), 3D spiral (molecular sea-serpent) (Alotaibi *et al.*, 2021), and antiferromagnet nanotubes (Grzelczak *et al.*, 2007). The progress in the fundamental of curvilinear antiferromagnetism as well as development of applications could position curvilinear antiferromagnets as a novel platform for the realization of geometrically tunable chiral antiferromagnets for antiferromagnetic spintronics, spin-orbitronics and magnonic devices relying on the geometrical curvature.

Application Viewpoint

Shapeable magnetoelectronics

Shapeable electronics includes flexible, printable, stretchable, and imperceptible systems; it has been enriched recently by magnetic functionality, forming a promising application direction where curvilinear magnetism is already applied. The concept of shapeable magnetoelectronics (Makarov *et al.*, 2016) unites several families of magnetoelectronic devices. Magnetoelectronics on flexible substrates allows the direct integration of giant magnetoresistive (GMR) devices onto bendable supports (Chen *et al.*, 2008), on-site conditioned flexible magnetoelectronics (Münzenrieder *et al.*, 2016), layered magnetic structures revealing GMR for the stretchable magnetoelectronics (Melzer *et al.*, 2011), printable magnetic sensorics (Makarov *et al.*, 2013), imperceptible magnetoelectronics (Melzer *et al.*, 2015a), and wearable magnetic field sensors forming wearable magnetoelectronics (Melzer *et al.*, 2015b). Shapeable material technologies (Makarov *et al.*, 2016; Karnaushenko *et al.*, 2019) allow to prepare complex 3D objects with applications to stretchable magnetic field sensorics (Karnaushenko *et al.*, 2015; Melzer *et al.*, 2020) (Fig. 3 (a)), energy storage devices (Gabler *et al.*, 2019). Shapeable magnetoelectronics devices found many applications as magnetosensitive electronics skins (e-skins) for augmented reality (Bermúdez *et al.*, 2018), geomagnetic field-driven artificial magnetoreception (Cañón Bermúdez *et al.*, 2018) (Fig. 3 (c)), interactive devices (Bermúdez and Makarov, 2021), touchless gauges (Melzer *et al.*, 2015a), mapping platforms (Melzer *et al.*, 2015b), multimodal magnetosensitive e-skins for m-MEMS (Ge *et al.*, 2019). Recently, a new approach to electric field controlled nanomagnets was proposed, which allows an electric field-induced deterministic switching between magnetic states without influencing intrinsic magnetic parameters (Volkov *et al.*, 2019b). Providing a possibility of tuning the magnetochiral properties of conventional magnetic materials using geometrical manipulations, this concept of artificial magnetoelectric materials should lead to a robust design of novel magnetoelectric devices.

Curvilinear spintronics

Today spintronics, including information processing and storage architectures rely on low-dimensional systems (Tsymbal and Zutic, 2019). The control of dynamics of topological magnetization textures by spin currents is the main issue of spintronics (Shinjo, 2009). The emergent field of curvilinear spintronics (or curved spintronics (Das *et al.*, 2019)), applies the main concepts of curvilinear magnetism to engineering of the motion of spin waves (curvilinear magnonics, see Section "Curvilinear magnonics"), domain walls, vortices, skyrmions (curvilinear skyrmionics, see Section "Curvilinear skyrmionics") by spin-orbit and spin-transfer torques. Current-driven transport problems of solitons in nanotubes already resulted in avoiding Walker breakdown (Yan *et al.*, 2010) and appearance of chiral breakdown (Landeros and Núñez, 2010; Yan *et al.*, 2012). The domain wall dynamics in bent nanostripes is accompanied by the emergence of a second Walker-like critical field, corresponding to the reorientation of the domain wall phase (Bittencourt *et al.*, 2021). Particular interest is applied to the magnetic vortex dynamics in spherical particles, including field-induced linear vortex dynamics in spherical shells (McKeever *et al.*, 2019), nutational dynamics of coupled vortices

(Lee *et al.*, 2017), resonantly excited precessional motion of a magnetic vortex core in soft magnetic spheres (Kim *et al.*, 2015). Domain wall dynamics in helix wires manifests the chirality sensitive domain wall mobility (Pylypovskyi *et al.*, 2016) (Fig. 3 (b)) and a negative mobility of the spin-torque driven domain wall (Yershov *et al.*, 2016). Among experimental realizations one has to mention curved nanowire spintronics for storage class memories and logic exploiting magnetic domain-wall logic (Allwood *et al.*, 2005; Luo *et al.*, 2020) (Fig. 3 (d)).

Curvilinear magnonics

Being a part of rapidly developing 3D magnonics (Gubbiotti, 2019; Barman *et al.*, 2021), curvilinear magnonics is an emergent applied field, which actively uses tailored 3D nanoarchitectures. 3D curved nanowires and curved nanosurfaces exhibit magnetic textures which are typically not observed in flat counterparts; they open new possibilities for the exploitation of magnons chirality and the resulting non-reciprocity of the magnon dispersion (Barman *et al.*, 2021). Curvilinear magnetic architectures enable to realize novel devices, such as ferromagnetic microtube ring resonators fabricated by rolling up layer system (Balhorn *et al.*, 2010), tunable spin-wave filters (Balhorn *et al.*, 2012), freestanding 3D magnon nanoresonators (Heyroth *et al.*, 2019), curved spin-wave lens (Toedt *et al.*, 2016) and family of on-chip rolled-up devices (Smith *et al.*, 2012). Channeling of spin waves with domain walls in curved waveguides was proposed in Garcia-Sanchez *et al.* (2015) and demonstrated experimentally (Wagner *et al.*, 2016). Engineered magnetic textures, in particular, on curved substrates, can be used for guiding, emitting and manipulating spin waves, which hint to possible future directions for technological prospects (Petti *et al.*, 2022). Recently, curvilinear magnetism has proposed several concepts, which seems to be prospective for 3D magnonics applications: a new type of magnonic crystals, curvature-induced ones, is proposed for ferromagnetic nanowires with periodically deformed shape (Korniienko *et al.*, 2019) (Fig. 3 (e)), magnonic waveguides with designer band gap spectrum (Tkachenko *et al.*, 2012), filtering of magnon spectrum based on bounding of spin waves by local bending of magnetic wire (Gaididei *et al.*, 2018), spin waves propagation over a distance ten times larger in the corrugated waveguide than in the planar waveguides (Turcan *et al.*, 2021), magnonic logic elements based on the nonreciprocity of the spin-wave spectrum in ferromagnet helix wires (Sheka *et al.*, 2015b), and nanotubes (Otálora *et al.*, 2016); (Otálora *et al.*, 2017), 3D nanovolcanoes (Fig. 2 (i)) as multi-mode microwave resonators with potential applications in telecom-frequency filters (Dobrovolskiy *et al.*, 2021), geometrically tunable magnon spectrum in antiferromagnetic nanohelix (Pylypovskyi *et al.*, 2020) (Fig. 3 (g)), flexible magnonic systems (Faurie *et al.*, 2021), spin-wave guiding in curved multimode waveguides (Wang *et al.*, 2021), 3D nanostructured lattices, 3D magnonic crystals and interconnects for a spin-wave computing (Chumak *et al.*, 2022).

Curvilinear skyrmionics

Magnetic skyrmions in curved geometries provide novel characteristics, new routes to stabilize, control their motion, which may promote the development of curvilinear skyrmionics (Liu *et al.*, 2022). Geometric stabilization of Néel skyrmions can be realized in magnets even without intrinsic DMI: small radius skyrmions can be stabilized by the extrinsic geometry-governed DMI in nanospheres (Kravchuk *et al.*, 2016), hemispherical caps (Yang *et al.*, 2021), and parabolic shells (Vilas-Boas *et al.*, 2015). As opposed, skyrmions of tunable radii are stabilized by the inhomogeneity of the curvature, they can be realized in nanoindentations (Pylypovskyi *et al.*, 2018). The concept of mesoscale DMI (see Section "Emergent Interactions") allows tuning skyrmion size in a wide range by geometrical manipulation, in particular, in nanospheres (Kravchuk *et al.*, 2016), bump structures (Kravchuk *et al.*, 2018; Korniienko *et al.*, 2020), in dome (antidome) structures (Carvalho-Santos *et al.*, 2020), cylindrical surfaces (Yershov *et al.*, 2022), nanotubes (Liu *et al.*, 2020), cylindrical nanostripes (Kechrakos *et al.*, 2020). A localized curvilinear defect can favor the multiplet of skyrmion states with a perspective to be utilized to encode and switch a bit of information (Kravchuk *et al.*, 2018). Reconfigurability of the skyrmion lattice on curvilinear defects (Fig. 1 (c3)) opens a new exciting perspective for the manipulation and control of spintronic devices relying on the topological Hall effect (Kravchuk *et al.*, 2018). Magnetic skyrmions on arrays of self-assembled nanodomains are perspective for the for magnetic recording applications (Tejo *et al.*, 2020).

Current-driven skyrmion motion in a nanotrack is affected by the Magnus force (the skyrmion Hall effect) (Chen, 2017). This effect is modified in a controlled way when the skyrmion moves along the curved part of the nanotrack (Cai and Liu, 2021), see Fig. 3 (i). Stable current-induced skyrmion propagation with a helical trajectory on magnetic nanotubes caused by the skyrmion Hall effect was predicted using micromagnetic simulations (Wang *et al.*, 2019) (Fig. 3 (h)). A possibility to tune current-induced skyrmion motion by geometrical manipulations can overcome the skyrmion Hall effect, which is essential for skyrmionics applications. Curvature-induced drift of the skyrmion is typically driven by the gradient of the local surface mean curvature. The skyrmion trajectory can be spiral if it moves around the bump (Korniienko *et al.*, 2020), or it can guide the skyrmion while traveling along the track (Carvalho-Santos *et al.*, 2021). The curvature-induced drift of a skyrmion essentially depends on the skyrmion type (Néel or Bloch skyrmion), while the trajectory of motion is determined by the type of the magnetic ordering (ferro- or antiferromagnetic) (Yershov *et al.*, 2022). The future challenge is to develop experimental works to observe skyrmion and control their dynamics in curved nanotracks (Liu *et al.*, 2022).

Magnetic soft robotics

Recent advances in mobile microrobotics (Sitti, 2017) selected magnetic soft robotics as a prospective direction novel emergent class of microrobot systems for various applications (Sitti and Wiersma, 2020). To the moment most of magnetically responsive flexible materials are magnetosensitive elastomers (Sitti and Wiersma, 2020; Chung *et al.*, 2020). Their magnetic properties are determined by the nonlocal magnetostatic interaction, providing a relatively large scale of the geometrical deformations. Novel

candidates for nanorobotics are organic and molecule-based magnets (Miller, 2014). Magnetic properties of such elastic ferromagnets are essentially influenced by local interactions (exchange, anisotropy, DMI), which enable size reduction of prospective devices in organic electronics and spintronics. The coupling between magnetic and mechanical subsystems in elastic ferromagnets can support spontaneous deformation of flexible enough planar film (or straight wire) induced by magnetic textures with such striking examples as soliton-induced deformation in cylindrical geometries (Dandoloﬀ *et al.*, 1995; Saxena *et al.*, 1998) and skyrmion-induced deformation in planar films (Kravchuk *et al.*, 2018). The shape transformation induced by inhomogeneous magnetization texture was predicted for flexible ferromagnetic rings (Gaididei *et al.*, 2019) and ribbons (Yershov *et al.*, 2019) (Fig. 3 (j)). The deformation is effectively controlled by the external magnetic field with possible applications for soft nanorobotics (Rus and Tolley, 2015) and soft magnetic sensorics (Wang *et al.*, 2018; Melzer *et al.*, 2020).

Magnetically actuated soft robots already found biomedical and environmental applications. This includes self-propelled micro-objects like magnetically capped magnetic surface walkers (Chen *et al.*, 2016) helical microswimmers (Chatzipirpiridis *et al.*, 2018), rod-like and tubular objects (Soto *et al.*, 2021). Janus micromotors can perform magnetically induced thermophoretic locomotion (Baraban *et al.*, 2013). 3D printed biodegradable helical microrobots with programmed magnetic anisotropy can pave the way to a new generation of small-scale robots for minimally invasive procedures (Gervasoni *et al.*, 2020). Magnetic soft robotics, in particular, swimming microrobots, grant promising new tools for in vivo applications, such as diagnosis and therapy in complex environments, microsurgies of individual cells, drug delivery, artificial fertilization techniques (Fig. 3 (k)), etc (Medina-Sánchez *et al.*, 2018; Magdanz *et al.*, 2020).

Closing Remarks

Curvilinear magnetism is a field that has balanced from the very beginning between fundamental research, material sciences, and technologies (Streubel *et al.*, 2016; Sander *et al.*, 2017; Fernández-Pacheco *et al.*, 2017; Fischer *et al.*, 2020; Vedmedenko *et al.*, 2020; Makarov *et al.*, 2022; Sheka, 2021; Sheka *et al.*, 2022a; Makarov and Sheka, 2022). Namely advances and synergy between fundamentals and applications, their complementary expertise stimulates the development of new theoretical methods, novel fabrication and characterization techniques as well as numerous applications exploring the utility of 3D-shaped curved magnetic architectures for shapeable magnetoelectronics, spintronics, magnonics, skyrmionics, and soft robotics.

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Iron Garnet Thin Films for Applications in Magnonics and Spintronics

Christian Holzmam and Manfred Albrecht, Institute of Physics, University of Augsburg, Augsburg, Germany

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Abstract

Iron garnets are an interesting class of material that continuously attracted strong research interest. They are ferrimagnetic insulators with a high Néel temperature (about 550K), exhibit a ultra-low Gilbert damping (as low as 10^{-5}), show strong magneto-optical response, and in some cases reveal uniaxial magnetic anisotropy and a magnetic compensation point. All these magnetic properties depend strongly on the rare-earth substitution, magnetoelastic or growth-induced anisotropy, film thickness, and stoichiometry. Therefore, single-crystalline garnet films of highest quality are nowadays the prime choice for studying all kinds of magnonic and spintronic effects like spin wave propagation, spin Hall effect, spin Seebeck effect, spin-orbit torques, or spin wave computing. This review describes the rich development of garnet thin films including the most recent developments in thin film preparation. Special attention is given to the tuning of the magnetic anisotropy as well as applications offered by garnet thin films.

Introduction

Garnets are a versatile material, whose value has been recognized for a long time. However, their usage was limited as natural gemstones for the most time being, dating back to at least 300 BCE (Schmetzer *et al.*, 2017). Only in the 1950s, the first magnetic garnets were synthesized (Bertaut and Forrat, 1956; Geller and Gilleo, 1957), which started research on a multitude of effects and applications over the next decades, leading to the recent developments as material for magnonics, spintronics, and opto-magnetic applications. While this review will focus on the tuning of the magnetic properties of garnet thin films suitable for modern spintronic applications, the rich history of garnets and their applications deserves a brief introduction.

In 1929, the structure of the garnet family was first refined, belonging to the cubic space group, with the composition identified as $A_3B_2C_3O_{12}$ (Menzer and der Granate, 1929). While most natural garnets are silicates with mainly Si atoms occupying the tetrahedral C sites, a wide range of atoms at the dodecahedral A (e.g., Ca, Mg, or Mn) and octahedral B sites (e.g., Al, Cr, or Sc) are known to naturally occur (Grew *et al.*, 2013), giving rise to a large natural color palette and explaining the garnets popularity as gems early on. More recently, due to their chemical stability and complex formation process, but nevertheless widespread occurrence in the earth's crust, natural garnets are exploited in petrochronology, trying to link the samples' specific properties to the environmental conditions like ambient temperature or pressure present at the time of the crystal growth (Baxter *et al.*, 2017). Furthermore, the hard and abrasive nature of natural garnets prompted their usage in water cutting, abrasive blasting, or sandpapers (Khan *et al.*, 2021), but the majority of modern research and technology is based on synthetic garnets, whose rise started in the 1950s, as depicted in Fig. 1.

With Louis Néel's theory of ferrimagnetism, formulated in 1948 (Neél, 1948), the search for new ferrimagnetic phases started. Shortly thereafter, in 1956, two independent groups synthesized the first (ferri-)magnetic iron garnets, namely yttrium (YIG), gadolinium (GdIG), and samarium (SmIG) iron garnets (Bertaut and Forrat, 1956; Geller and Gilleo, 1957). The distinctive magnetic properties of especially YIG were quickly recognized, and research on these new type of magnetic material started off. In particular, the extremely narrow ferromagnetic resonance absorption line at GHz frequencies prompted studies on the integration of garnets in microwave devices (Belov and Zaitseva, 1958). First theoretical and experimental studies in the 1960s were based on bulk YIG disks (Damon and Van De Vaart, 1965), while later on thin films grown by liquid phase epitaxy were in the focus (Coeure, 1985). Magnetostatic waves in the microwave regime propagating in garnet disks or films were envisioned as microwave delay lines, filters, or limiters (Adam, 1988; Ishak, 1988). While garnet-based devices offer a low microwave propagation loss and tunability by a magnetic bias field and are of small size, the higher bandwidth and accuracy of the upcoming surface - and later on bulk - acoustic wave (SAW) technology made the magnetostatic wave-based technology less attractive (Adam, 1988). However, more recently, the higher frequency bands used in the 5G standard are challenging for SAW filters, (Mahon, 2017) which prompts research of alternate technologies, including microwave photonics (Marpaung *et al.*, 2019) as well as once again using magnetostatic waves in garnets for microwave signal processing (Dai *et al.*, 2020).

Furthermore, around the 1960s, laser technology started getting attention, and it was realized that crystalline garnets like yttrium aluminum garnets (YAG) are an ideal laser host material with high heat dissipation. Using Nd^{3+} ions as emitter, the Nd:YAG laser was first developed in 1964 (Geusic and Marcos, 1964) and continuously improved over the next decades, and is still to date one of the most utilized laser systems (Hecht, 2010).

Concurrently, the search for fast and reliable memory devices in the early 1960s provoked the concept of the magnetic bubble memory (O'Dell, 1986). After initial experimental and theoretical work on orthoferrites and hexaferrites proved to be less promising (Nielsen, 1976), the search for a suitable bubble host material began. To achieve the bubble state, an out-of-plane easy axis of magnetization is required, and therefore the uniaxial magnetic anisotropy K_u has to overcome the demagnetizing energy $\frac{\mu_0}{2} M_s^2$ in thin films, with the saturation magnetization M_s . At the same time, the bubble diameter is proportional to $\propto 1/M_s^2$ and the mobility to $\propto 1/\alpha$, where α is the magnetic damping parameter (O'Dell, 1986; Nielsen, 1976; Giess, 1980). Garnets, with comparatively low M_s and α , proved to be a promising material choice, enabling sub-micrometer bubbles (Coeure, 1985; Giess, 1980), e.g., by tuning M_s by Fe^{3+} substitutions with nonmagnetic ions like Sc^{3+} or Ga^{3+} , but only the discovery of the growth-induced anisotropy enabled the design of garnets with perpendicular magnetic anisotropy (Bobbeck *et al.*, 1970). In such systems, preferential ordering during the garnet growth causes the uniaxial magnetic anisotropy. This preferential ordering was induced by

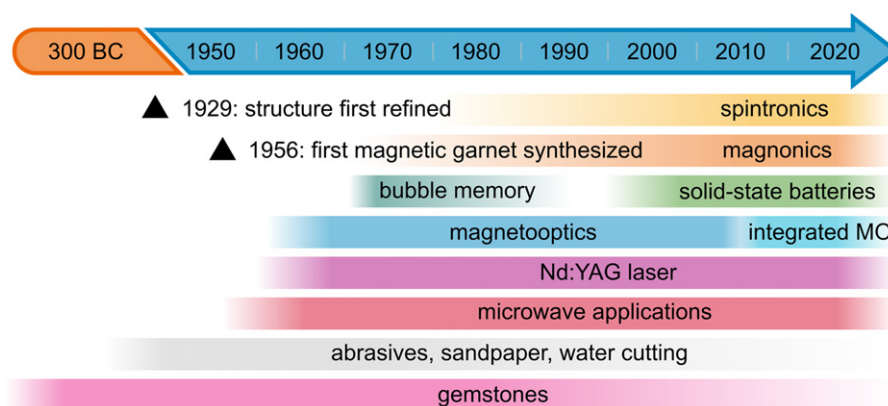


Fig. 1 Timeline showing the different research areas utilizing garnets.

mixing (rare-earth, RE) ions of different sizes, mainly on the dodecahedral sites, e.g., combining larger Sm^{3+} and smaller Lu^{3+} ions. The excellent single crystalline growth of the (substituted) garnets on readily available gadolinium gallium garnet (GGG) substrates and the tunable magnetic properties promised ideal prerequisites for bubble memory devices. Therefore, bubble memory research was almost exclusively focused on garnet systems, and later on also on amorphous alloys such as Gd-Co (Nielsen, 1976). However, the progress in semiconductor technology rendered bubble memories noncompetitive, and research seized in the late 1980s (Kang *et al.*, 2016). However, its principle is still pursued, owing to the progress in, e.g., racetrack memory using chiral spin objects like (anti-) skyrmions (Parkin *et al.*, 2008; Fert *et al.*, 2013; Woo *et al.*, 2016; Heigl *et al.*, 2021).

In the meantime, another property of the garnets attracted interest - their strong magneto-optical response in form of the Faraday and Cotton-Mouton effect connecting their magnetic and optic properties. Especially Bi-, Pb- or Ce- substituted garnets exhibit a large Faraday rotation and low optical absorption in the near-infrared range (Hansen and Krumme, 1984). Early on, the possibilities of such garnets for magneto-optical memories using thermomagnetic writing and optical readout or in combination with polarizers as displays were recognized, (Coeure, 1985; Paroli, 1984; Scott and Lacklison, 1976) and in 1982 the light switching array (LISA) was commercially available (Hansen and Tolkendorf, 1982). It consisted of a patterned garnet array close to the compensation temperature, which acted like pixels, switchable by small magnetic fields and local heat pulses, driving the garnet through the compensation point and therefore changing the light polarization. Bubble magneto-optical displays combined the bubble and magneto-optical technology in a way that bubbles were used as individual pixels (Paroli, 1984).

Lately, progress in growing garnets on non-matching substrates like silicon by an annealing or wafer bonding processes enabled the development of monolithically integrated magneto-optical devices based on Bi- or Ce- doped garnets on widely used Si-waveguides (Shoji and Mizumoto, 2014; Stadler and Mizumoto, 2014; Srinivasan and Stadler, 2022). While data transfer via optical fibers offers high speed, optical components like isolators and circulators are required. As the garnets offer the highest known Faraday rotation to optical absorption ratio in the NIR regime, which contains the main bands used for optical communications, (Stadler and Mizumoto, 2014; Srinivasan and Stadler, 2022) the design of highly efficient optical isolators or circulators is possible, e.g., using Mach-Zehnder modulators or ring resonators. Isolation ratios of about 30 dB with insertion losses of about 5 dB are already demonstrated (Srinivasan and Stadler, 2022; Zhang *et al.*, 2019a). However, the integration of high-quality garnets on silicon waveguides in a cost-efficient and compatible way with semiconductor technology is still challenging and under active research (Srinivasan and Stadler, 2022; Fakhrol *et al.*, 2021).

While most of the current research on garnets is driven by either their distinct magnetic properties or their magneto-optic response, non-magnetic Li-based garnets gained recently a lot of attention as material for solid-state batteries (Cheng *et al.*, 2017; Gao *et al.*, 2018; Thangadurai *et al.*, 2014). The most widespread used batteries rely on Li-ions, but metallic Li offers significantly higher energy densities. However, in conventional liquid electrolyte batteries, the growth of dendrite structures causes short circuits when trying to use metallic Li electrodes (Cheng *et al.*, 2017; Gao *et al.*, 2018; Chen *et al.*, 2022). In contrast, solid-state electrolytes solve this issue, and the Li-rich garnet $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ was found to exhibit high ion, but low electrical conductivity, while being chemically stable over a wide temperature range, and is for these reasons considered as a promising candidate for a next-gen battery (Gao *et al.*, 2018; Thangadurai *et al.*, 2014).

During the last decades, (Arsad *et al.*, 2023) the unique magnetic properties of the garnets including the ferrimagnetic structure, the low spin wave damping and high Néel temperature (Schmidt *et al.*, 2020), as well as their insulating nature combined with advanced deposition techniques of single crystalline thin films sparked interest in the investigation of a multitude of magnonic and spintronic effects (Serga *et al.*, 2010; Csaba *et al.*, 2017; Dieny *et al.*, 2020; Yang *et al.*, 2021a; Avci, 2021; Stupakiewicz and Satoh, 2021; Pirro *et al.*, 2021; Barman *et al.*, 2021; Kim *et al.*, 2022; Mahmoud *et al.*, 2020). While spin waves in garnets and their quanta representation - the magnons - were historically used in analog microwave signal processing, spin wave propagation was already studied as early as in the 1960s (Eshbach, 1962) and their potential as information carriers was soon after recognized (Serga *et al.*, 2010; Hillebrands and Ounadjela, 2003). Therefore, the excitation and propagation of spin waves, along with their unique magnetic properties like magnetic anisotropy, magnon non-reciprocity, and negative group velocity, or external tunability, has been and is currently extensively studied, e.g., for small-footprint and low energy information transmission and storage (Serga *et al.*, 2010; Pirro *et al.*, 2021; Barman *et al.*, 2021;

Sheng *et al.*, 2021; Chumak *et al.*, 2022), the interaction of magnons with magnetic textures (Yu *et al.*, 2021), or more recently information processing in spin wave-based neuromorphic computing (Csaba *et al.*, 2017; Pirro *et al.*, 2021; Mahmoud *et al.*, 2020; Chumak *et al.*, 2022; Rana and Otani, 2019).

In addition, bilayers consisting of a magnetic garnet and a conducting layer, typically a heavy metal like Pt or W, are studied in the field of spintronics. Due to the antiferromagnetic coupling of multiple magnetic sublattices in garnets, garnet/metal bilayers are a model system to study ferrimagnetic spintronics (Yang *et al.*, 2021a; Kim *et al.*, 2022; Zhou *et al.*, 2021a; Chumak *et al.*, 2015). Consequently, a multitude of effects are extensively investigated, including transport effects like spin wave generation and motion by spin-pumping, spin-orbit torques, or the spin Seebeck effect (Yang *et al.*, 2021a; Avci, 2021; Barman *et al.*, 2021; Fulara *et al.*, 2019; Demidov *et al.*, 2020; Uchida *et al.*, 2008, 2010a), spin to charge current inter-conversion by the (inverse) spin Hall effect, ultrafast domain wall motion, and implications for information storage and manipulation (Dieny *et al.*, 2020; Yang *et al.*, 2021a; Stupakiewicz and Satoh, 2021; Trier *et al.*, 2022; Brataas *et al.*, 2020; Hirohata *et al.*, 2020).

In this review, the focus is on tuning the magnetic properties of rare-earth iron garnet thin films, providing a base material suitable for magnonic and spintronic applications. In this regard, a short introduction to the structure and properties of bulk garnets (chapter 2) and common growth techniques of thin films (chapter 3) is given. Afterward, the wide range of tunable magnetic properties is presented in chapter 4, leading to possible applications of iron garnet thin films as discussed in chapter 5.

Structure and Magnetic Properties of Iron Garnets

Garnets have a cubic but rather complex unit cell, as depicted in Fig. 2(a). They belong to the space group $Ia\bar{3}d$ and host eight formula units of $C_3A_2D_3O_{12}$ per unit cell. For the rare-earth iron garnets (REIGs), Fe^{3+} ions sit at both the octahedral (Wyckoff position 16a) as well as the tetrahedral sites (Wyckoff position 24d), while the rare earth ions RE^{3+} form a dodecahedral coordinated sublattice (Wyckoff position 24c). The garnets unit cell lattice parameter a follows the rare earth ionic radii, as shown in Fig. 2(e). Additionally, the large unit cell can host substitutions on all lattice sites, with large substituents preferentially occupying the dodecahedral spaces. However, the RE ions larger than samarium are generally too large, e.g., NdIG is expected to have a cubic lattice constant of 12.60 Å, but is thermodynamically unstable (Espinosa, 1962). Furthermore, iron substitutions are mainly driven by the ionic radii of the substituent, as smaller ions prefer the octahedral sites (Gilleo and Geller, 1958; Geller, 1967), but only a few ions favor a tetrahedral coordination (Milam-Guerrero *et al.*, 2021).

The magnetic moments of the iron and RE ions form three magnetic sublattices, corresponding to the three crystallographic sites. The two Fe^{3+} sublattices are aligned antiferromagnetically, coupled by a strong superexchange interaction transmitted by the oxygen ions. Due to the imbalance of the two sites by 3:2, ferrimagnetic ordering with a net moment of one iron atom ($5m_B$) results (Nakamoto *et al.*, 2017).

For the RE sublattice, the superexchange interaction with the tetrahedral Fe^{3+} sublattice is dominant (Bayaraa *et al.*, 2019), which leads to an antiferromagnetic alignment of the spin moment S of the RE sublattice and the net iron sublattice. For the

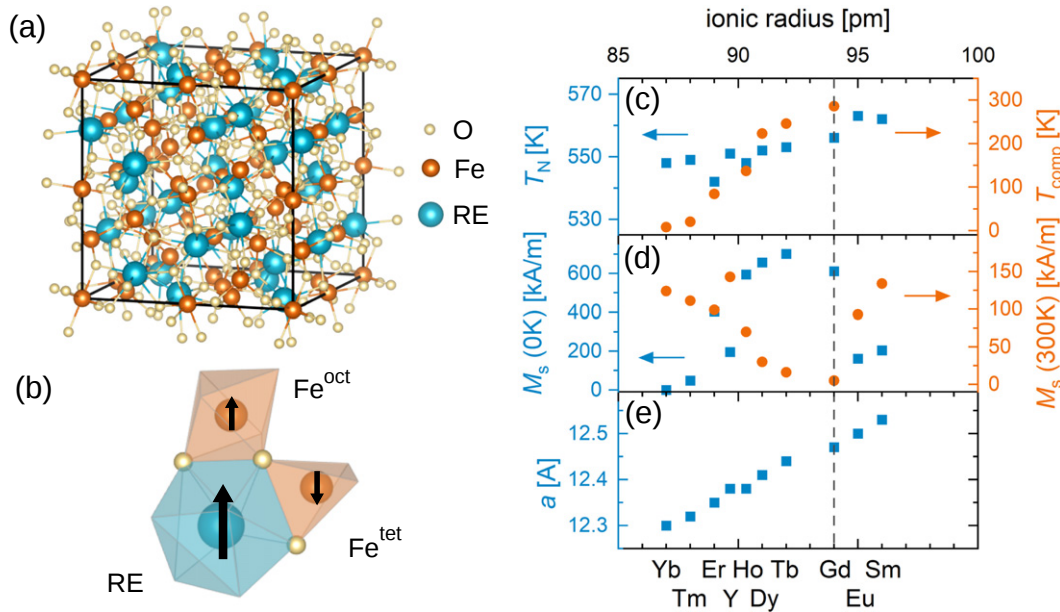


Fig. 2 (a) Iron garnet unit cell, designed using VESTA3 (Momma *et al.*, 2011). (b) Alignment of the magnetic sublattices for the heavier RIGs. (c-e) Iron garnet bulk properties in dependence of the ionic radius of the rare earth ion for different dodecahedral substitutions, based on Table 1.

Table 1 Lattice constant a , saturation magnetization M_S (at 0 K and room temperature (RT)), Ne’el temperature T_N , compensation temperature T_{comp} , first-order cubic magnetocrystalline anisotropy K_1 , magnetostriction constant λ , Gilbert damping parameter α , and Faraday rotation θ_F (at a wavelength of 600 nm) for selected iron garnets. Unless otherwise stated, all data is given at room temperature for bulk garnets. α was extracted from thin film samples (thickness < 100 nm)

	a [$\text{\AA}$]	M_S (0 K) [$\frac{\text{kA}}{\text{m}}$]	M_S (RT) [$\frac{\text{kA}}{\text{m}}$]	T_N [K]	T_{comp} [K]	K_1 [$\frac{\text{kJ}}{\text{m}^3}$]	λ_{100} [10^{-6}]	λ_{111} [10^{-6}]	α [10^{-3}]	θ_F [$10^3 \frac{^\circ}{\text{cm}}$]
YbIG	12.30	0	124	548	< 8	− 0.61	1.4	− 4.5		
TmIG	12.32	48	111	549	< 20	− 0.58	1.4	− 5.2	15	
ErIG	12.35	402	99	542	84	− 0.6	2.0	− 4.9		0.6
YIG	12.38	196	143	551	/	− 0.61	− 1.4	− 2.4	0.06	1.2
HoIG	12.38	594	70	548	137	− 0.5	− 3.4	− 4.0		
DyIG	12.41	656	30	552	223	− 0.5	− 12.5	− 5.9	230	1.5
TbIG	12.44	701	16	553	246	− 0.82	− 3.3	12		2.4
GdIG	12.47	611	5	556	286	− 0.41	0	− 3.1	10	1.6
EulG	12.50	162	93	563	/	− 3.8	21	1.8	20	0.9
SmlG	12.53	204	134	562	/	− 1.74	21	− 8.5		
BiIG	12.62		115		/	0.76		− 4.6		> 60
	(Popova <i>et al.</i> , 2012; (Geller <i>et al.</i> , (Popova <i>et al.</i> , (Hellwege, (Geller <i>et al.</i> , 1965; (Okuda <i>et al.</i> , 1990; (Iida, 1967) (Ciubotariu <i>et al.</i> , 2019; (Hansen and Krumme, 1984; Okuda <i>et al.</i> , 1990)									
	(Espinosa, 1962) 1963, 1965) 2012; Hellwege, 1978; Okuda <i>et al.</i> , 1990) 1978; Below <i>et al.</i> , 1967) Henderson and White, 1961; Pauthenet, 1958; Geschwind and Walker, 1959) Wu <i>et al.</i> , 2018; Hauser <i>et al.</i> , 2016; Bauer <i>et al.</i> , 2020; Rosenberg <i>et al.</i> , 2018; Ortiz <i>et al.</i> , 2021a; Okuda <i>et al.</i> , 1990; Iida, 1967)									

Note: Bulk BiIG is not thermodynamically stable, but can be epitaxially grown as thin film (Popova *et al.*, 2012).

heavier RE (Gd-Yb) with more than half filled 4f orbitals, spin S and angular momentum L are parallel (according to Hund's rules), and therefore the RE sublattice and the net iron sublattice are aligned antiparallel. This gives rise to three coupled magnetic sublattices, as depicted in Fig. 2(b), resulting in a total magnetic moment $m_{\text{tot}} = m_{\text{Fe}^{\text{tet}}} - m_{\text{Fe}^{\text{oct}}} - m_{\text{RE}}$. Typically, at low temperatures, the magnetic moment of these garnets is dominated by the RE sublattice, while at room temperature the moment is iron-dominant, due to the weaker intra- and interatomic coupling of the RE sublattice (Geller *et al.*, 1965; Bayarar *et al.*, 2019; Copland, 1970). Fig. 2(d) shows the evolution of the magnetization at 0K and 300K for the rare-earth garnets (see also Table 1). Consequently, in some cases a compensation point at T_{comp} is present, at which the Fe^{3+} and RE^{3+} magnetic moments are balanced, e.g., for GdIG at about 286K (Geller *et al.*, 1965). In the special cases of YbIG and TmIG, a bulk T_{comp} at low temperatures close to 0K is expected, while for thin films higher compensation temperatures up to 80K are reported (Shao *et al.*, 2019a). Such compensated garnets enable the study of an effectively antiferromagnetic material with spin resonances in the THz regime (Zhou *et al.*, 2021a), while probing the individual magnetic sublattices at the same time (Kim *et al.*, 2022).

On the other hand, the spin and angular moment of the lighter REs with less than half filled 4f shells are antiparallel in the ground state. Therefore, while the RE spin moment is coupled antiparallel to the net iron sublattice by the superexchange interaction, the angular moment is parallelly aligned, which leads to a more complex picture. For SmIG, a dominating orbital contribution leads to a parallel alignment of the total Sm^{3+} and Fe^{3+} moments up to a crossover temperature between 100 and 330K. For higher temperatures, the spin moment dominates, which leads to a contribution opposing the net Fe^{3+} moment (Geller *et al.*, 1963; van Loef, 1968; Guillot *et al.*, 1983). A similar behavior is expected for the garnets with REs lighter than Sm (Geller *et al.*, 1963). However, EuIG shows an antiparallel alignment of the Eu^{3+} and Fe^{3+} sublattices at all temperatures below T_N due to the population of excited Eu^{3+} states, which are close in energy to the ground state (Geller *et al.*, 1963; Wolf and Vleck, 1960; Myers *et al.*, 1968). However, in all cases, no compensation temperature is observed.

Furthermore, all garnets possess a similar Néel temperature of about 550K (Hellwege, 1978), governed by the strongly coupled iron sublattices, but greatly varying compensation temperatures (see Fig. 2(c) and Table 1), extending from almost room temperature for GdIG to close to 0K for YbIG, or no compensation point at all.

The garnets' popularity as a system to study magnonics is commonly explained by their insulating nature with a typical band gap in the range of 2.3 – 2.8 eV (Nakamoto *et al.*, 2017; Deb *et al.*, 2013; Metselaar and Larsen, 1974), next to their low spin-wave damping. YIG is especially known for its ultra-low Gilbert damping α . For thin films below 100 nm values as low as 6×10^{-5} are reported (Schmidt *et al.*, 2020; Hauser *et al.*, 2016). This is accompanied by low microwave losses and small ferromagnetic resonance linewidths. Furthermore, substituting Y with other REs enables easy tuning of the magnetic properties like magnetic anisotropy or compensation temperature, however, in most cases it increases the damping by about two orders of magnitude (see Table 1).

Finally, the REIGs possess a large Faraday rotation θ_F , especially for Bi or Ce substituted garnets. Similarly to NyIG, these garnets are not a-priori thermodynamically stable, but have been grown as epitaxial thin films (Popova *et al.*, 2012). However, more often, partially Bi- or Ce-substituted REIGs are studied (Zhang *et al.*, 2019a; Fakhrul *et al.*, 2021; Huang *et al.*, 2017; Levy *et al.*, 2019; Stadler and Hutchings, 2018), combining properties from different garnet types and achieving high Faraday rotations, e.g., up to $6000 \frac{\circ}{\text{cm}}$ for Bi- or Ce-doped TbIG thin films at a wavelength of 1550 nm (Fakhrul *et al.*, 2021).

Growth of Iron Garnet Thin Films

High-quality single crystalline iron garnet thin films with low spin-wave damping, presence of a compensation point, perpendicular magnetic anisotropy (PMA), and smooth surfaces are typically achieved by epitaxial growth on nearly lattice-matching substrates. Most commonly, non-magnetic gadolinium gallium garnets (GGG) or various substituted GGG garnets, as listed in Table 1, are used as substrates.

These substrates possess the same structure and a closely matching lattice parameter compared to the REIGs, e.g., a lattice mismatch of less than 0.1% for YIG on GGG. Using GGG as a substrate, pseudomorphic growth of a wide variety of iron garnets has been reported, including YIG (Hauser *et al.*, 2016; Kang *et al.*, 2005; Manuilov *et al.*, 2009; Onbasli *et al.*, 2014; Krysztofik *et al.*, 2021a), TmIG (Ciubotariu *et al.*, 2019; Wu *et al.*, 2018; Quindeau *et al.*, 2017), TbIG (Rosenberg *et al.*, 2018; Ortiz *et al.*, 2018), and GdIG (Geprägs *et al.*, 2016; Maier-Flaig *et al.*, 2017; Holzmann *et al.*, 2022). Hereby, different growth methods are applied, but most commonly pulsed laser deposition (PLD), RF magnetron sputtering, or liquid phase epitaxy (LPE) are utilized. While all three techniques are suitable to grow high-quality films, PLD (Ciubotariu *et al.*, 2019; Hauser *et al.*, 2016; Rosenberg *et al.*, 2018; Manuilov *et al.*, 2009; Onbasli *et al.*, 2014; Quindeau *et al.*, 2017; Ortiz *et al.*, 2018; Holzmann *et al.*, 2022; Jung *et al.*, 2022) and sputtering (Wu *et al.*, 2018; Kang *et al.*, 2005; Lustikova *et al.*, 2014; Ding *et al.*, 2020a) yield films in the thickness range of several to hundreds of nm, as for thicker films in the μm range, LPE is preferred (Maier-Flaig *et al.*, 2017; Aichele *et al.*, 2003; Guo *et al.*, 2016). However, recently, also high-quality thin films with sub-100 nm thicknesses were successfully grown by LPE (Pirro *et al.*, 2014; Dubs *et al.*, 2017; Rao *et al.*, 2018; Dubs *et al.*, 2020).

To achieve the crystallization of the garnet phase during PLD or sputter deposition, films are usually grown from bulk garnet targets at elevated temperatures at around 500 – 900°C in an oxygen-containing atmosphere (Ciubotariu *et al.*, 2019; Rosenberg *et al.*, 2018; Manuilov *et al.*, 2009; Onbasli *et al.*, 2014; Quindeau *et al.*, 2017; Ortiz *et al.*, 2018; Holzmann *et al.*, 2022). Usually, no further annealing is necessary. Using this approach, thin films of excellent quality can be achieved. However, room-temperature garnet deposition followed by post-deposition annealing were shown to yield films of matching quality. Hereby, varying annealing temperatures (typically between 600 – 1200°C) and times (few minutes to several hours) are applied to the as-deposited amorphous films (Hauser *et al.*, 2016; Kang *et al.*, 2005; Krysztofik *et al.*, 2021a; Ding *et al.*, 2020a). After annealing, single crystalline films can be obtained revealing damping parameters as low as 6×10^{-5} with FMR linewidths of $m_0 \Delta H_{\text{FWHM}} \approx 260 \text{ mT}$ at 9.6 GHz as reported for

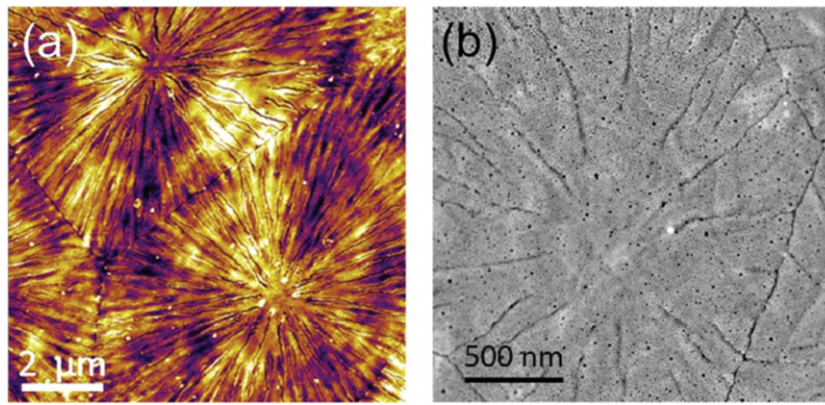


Fig. 3 (a) AFM and (b) TEM image of DyIG films after annealing at 950°C for 5 min, showing a distinct grain structure with cracks. The images were recorded using (a) a 38 nm thick film grown on an Si substrate and (b) a 22 nm thick film grown on a Si³N⁴ membrane. Reproduced with permission from Bauer, J.J., Rosenberg, E.R., Kundu, S., *et al.*, 2020. Dysprosium iron garnet thin films with perpendicular magnetic anisotropy on silicon. *Advanced Electronic Materials* 6 (1), 1900820. <https://doi.org/10.1002/aelm.201900820>, © 2020, WILEY VCH.

a 56 nm thick YIG film on GGG (Hauser *et al.*, 2016). In this study, these reported values were even lower than for comparable films grown by PLD at elevated temperatures. Note that films grown by sputtering typically show comparable Gilbert damping, but a slightly increased FMR linewidth (e.g., $m_0\Delta H_{\text{FWHM}} \approx 660$ mT at 9.45 GHz for a 96 nm thick YIG/GGG sample (Schmidt *et al.*, 2020; Lustikova *et al.*, 2014), but offering better scalability for potential applications.

During the last years, the growth of iron garnet thin films on non-matching but technology-relevant substrates like silicon or glass has prompted a lot of research activities, e.g., for the integration in photonic circuits as optical isolators or circulators (Srinivasan and Stadler, 2022; Zhang *et al.*, 2019a; Sun *et al.*, 2015; Zhang *et al.*, 2019b; Shoji and Mizumoto, 2019). For this, two main routes were developed. Monolithic growth on various substrates was achieved using post-deposition annealing, including rapid thermal annealing (RTA) processes (Zhang *et al.*, 2019a; Bauer *et al.*, 2020; Sun *et al.*, 2015; Zhang *et al.*, 2019b). For YIG films on Si/SiO_x, an annealing temperature in the range of 700 – 900°C for several minutes up to several hours (Zhang *et al.*, 2015; Bhoi *et al.*, 2018; Krysztofik *et al.*, 2021b) or RTA at 800 – 900°C for 3 – 5 minutes (Fakhrul *et al.*, 2021; Bi *et al.*, 2011) are commonly used. However, the annealing process is often accompanied by crack formation in the thin film, developing mainly during the cooling process due to different thermal expansion coefficients of the garnet film ($\approx 2 \times 10^{-5}$ 1/K (Geller *et al.*, 1969)) and the substrate ($\approx 3 \times 10^{-6}$ 1/K for Si (Okada and Tokumaru, 1984)). Examples of the film morphology of DyIG thin films grown on Si and Si³N⁴ substrates revealing oriented lateral grain growth and crack formation after annealing are presented in Fig. 3. Furthermore, the large lattice mismatch between the garnet and for example silicon causes polycrystalline film textures (Bauer *et al.*, 2020; Sun *et al.*, 2015; Zhang *et al.*, 2015), not fully matching the properties of high-quality single-crystals. On the other hand, single crystalline garnet thin films grown on matching substrates were successfully transferred or bonded to other substrates using for example wafer bonding, exfoliation, or epitaxial lift-off processes, which could offer an alternative route to realize single crystalline garnet films on any substrates (Srinivasan and Stadler, 2022; Shoji and Mizumoto, 2019; Bi *et al.*, 2011; Kum *et al.*, 2020).

Tuning of the Magnetic Properties of Iron Garnet Thin Films

One characteristic feature of iron garnet thin films grown epitaxially on suitable substrates is the ability to tune their magnetic properties to fit the desired specifications, including the magnetic anisotropy, saturation magnetization, or compensation temperature. On the one hand, the choice of the rare earth element has a huge impact on the magnetic properties, but on the other hand growth- or strain-induced effects, film thickness and stoichiometry, as well as interface effects are employed to fine-tune the magnetic properties. For example, controlling the magnetic anisotropy is of great importance for many magnonic and spintronic applications, and in particular garnet films with PMA are of great interest. Therefore, the evolution of the magnetic anisotropy with different film parameters is a well-studied topic, which will be discussed in the following.

The magnetic anisotropy of a thin film is governed by the effective magnetic anisotropy K_{eff} , which consists of several individual contributions. By convention, a positive $K_{\text{eff}} > 0$ denotes a system preferring an out-of-plane alignment of the magnetic moments. For thin films, the magnetic shape anisotropy K_s tries to minimize the dipolar energy of the system by aligning the magnetic moments in the in-plane direction, which depends on the saturation magnetization M_s as

$$K_s = -\frac{\mu_0}{2} M_s^2. \quad (1)$$

To achieve PMA, other contributions have to overcome K_s . For crystalline films, the magnetocrystalline anisotropy gives an anisotropy contribution depending on the crystal symmetry. In the case of the cubic garnet structure, an alignment of the magnetic moments along the $\langle 111 \rangle$ crystallographic directions is preferred. Parenthetically, garnet thin films are most often grown on

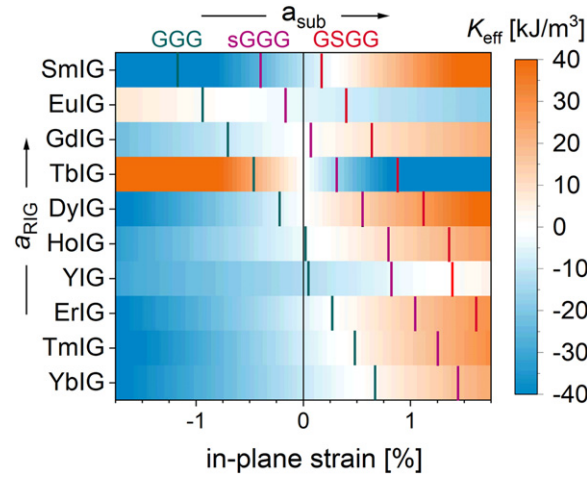


Fig. 4 Theoretical calculation of the effective magnetic anisotropy (K_{eff}) values in dependence of the in-plane strain in fully strained pseudomorphic REIG thin films. The colored lines indicate the expected strain for growth on commonly used substrates GGG ($a = 12.383 \text{ \AA}$), sGGG ($a = 12.500 \text{ \AA}$), or GSGG ($a = 12.570 \text{ \AA}$). $K_{\text{eff}} > 0$ denotes a preferred out-of-plane magnetic easy axis.

(111) oriented substrates, but also (001) oriented substrates are occasionally used, e.g., if the magnetostriction is stronger along the [001] direction. However, in most cases the first order cubic magnetocrystalline anisotropy constant K_1 is negligibly small at room temperature ($< 1 \frac{\text{kJ}}{\text{m}^3}$, see [Table 1](#)) and insufficient to overcome K_s .

On the contrary, the magnetoelastic anisotropy K_s connects the magnetic with the elastic properties of the thin film. A lattice distortion of the crystalline unit cell induces a reorientation of the electronic orbitals, which is coupled to the magnetic moments via spin-orbit interaction. By growing films under a small in-plane lattice mismatch $\varepsilon_{||} = (a_{\text{film, strained}} - a_{\text{film, relaxed}}) / a_{\text{film, relaxed}}$, a strain $\sigma_{||} = \frac{Y}{1-\nu} \varepsilon_{||}$ is induced, which consequently causes K_s , as expressed by ([Hansen, 1978](#); [Quindeau et al., 2017](#); [Fu et al., 2017](#); [Sokolov et al., 2016](#))

$$K_s = -\frac{3}{2} \lambda_{111} \sigma_{||}. \quad (2)$$

The elastic properties of the sample are given by the Young's modulus Y , the Poisson ratio ν , and the magnetostriction constant λ_{111} .

Furthermore, for mixed garnets, which contain a mixture of different RE elements, a further growth-induced anisotropy K_g can be present. The large garnet unit cell offers unequal crystallographic sites, and different cations will preferentially occupy certain sites during thin film growth, mainly driven by the cation ionic radius. Caused by this asymmetry, an additional magnetic anisotropy contribution K_g can be introduced ([Gyorgy et al., 1973](#); [Callen, 1971](#)).

Altogether, these contributions sum up to

$$K_{\text{eff}} = K_s + K_g + \frac{K_1}{12}. \quad (3)$$

[Eqs. \(1–3\)](#) and using the corresponding bulk values (see [Table 1](#)) allow estimating the different contributions to K_{eff} for different REIG thin films. Hereby, only pure garnets ($K_g = 0$) are considered, and fully strained pseudomorphic films with ([Geprägs et al., 2016](#)) growth direction are assumed. [Fig. 4](#) shows K_{eff} in dependence of an in-plane lattice mismatch $\varepsilon_{||}$. Additionally, the expected strain for films grown on commonly used substrates is marked by colored lines, including GGG, sGGG, and GSGG (see also [Table 2](#)). As EuIG and TbIG possess positive magnetostriction ($\lambda_{111} > 0$), compressive in-plane strain ($\varepsilon_{||} < 0$) promotes a magnetoelastic anisotropy favoring PMA, while for all other shown garnets, tensile in-plane strain ($\varepsilon_{||} > 0$) is necessary to favor PMA due to their negative magnetostriction ($\lambda_{111} < 0$). These findings have been validated in numerous experimental works, e.g., comparing EuIG and GdIG thin films grown on (111) oriented GGG substrates, where PMA has been reported for the EuIG/GGG films ([Rosenberg et al., 2018](#); [Ortiz et al., 2018](#)), but not for GdIG/GGG films ([Holzmann et al., 2022](#)). While in both cases, the films exhibit a compressive in-plane strain, only the positive magnetostriction of EuIG leads to a magnetoelastic anisotropy favoring PMA. However, there is a huge difference in the potency of the magnetoelastic anisotropy depending on the RE species. On the one hand, λ_{111} varies for the different REIGs, and on the other hand, a strongly rare earth-dependent magnetization causes a varying K_s . Thus, in the following section a summary of the magnetic properties for different REIG thin films is presented.

YIG Yttrium iron garnet (YIG) has a rather low λ_{111} of -2.4×10^{-6} and high saturation magnetization of $143 \frac{\text{kA}}{\text{m}}$ at room temperature, which makes it difficult to control the magnetic anisotropy and achieve PMA solely by magnetostriction. It was reported that a tensile lattice mismatch $\varepsilon_{||} > 1\%$ is necessary to achieve PMA in 10 nm thick YIG films, e.g., grown on either GSGG or GSGG substrates, but already for 15 nm thick films the PMA vanished, as shown in [Fig. 5](#) ([Li et al., 2019](#)). However, additional buffer layers can help to suppress strain relaxation, and for a trilayer system SmIG/YIG/SmIG with SmIG buffer layers, PMA was maintained up to a YIG thickness of 40 nm ([Fu et al., 2017](#)). Furthermore, the recrystallization of amorphous films with a large lattice mismatch by post-deposition annealing can lead to films with locally different strain levels and a tilted magnetic easy axis, as reported for YIG ([Krysztófik et al., 2021a](#)), and later on for different REIG films ([Liu et al., 2022](#)).

Table 2 Composition and lattice constant a of commonly used garnet substrates

Substrate	Composition	a [Å]
YAG	$\text{Y}_3\text{Al}_5\text{O}_{12}$	12.005
GGG	$\text{Gd}_3\text{Ga}_5\text{O}_{12}$	12.383
YSGG	$\text{Y}_3(\text{Sc}_2\text{Ga}_3)\text{O}_{12}$	12.470
sGGG	$(\text{Gd}_{2.6}\text{Ca}_{0.4})$	12.500
GYSGG	$(\text{Ga}_{4.1}\text{Mg}_{0.25}\text{Zr}_{0.65})\text{O}_{12}$	12.507
GSGG	$(\text{Gd}_{0.63}\text{Y}_{2.37})(\text{Sc}_2\text{Ga}_3)\text{O}_{12}$	12.570

Note: Li, G., Bai, H., Su, J., *et al.*, 2019. Tunable perpendicular magnetic anisotropy in epitaxial $\text{Y}_3\text{Fe}_5\text{O}_{12}$ films. *Applied Physics Letters Materials* 7 (4), 041104. <https://doi.org/10.1063/1.5090292>. Zanjani, S.M., Onbaşlı, M.C., 2020. Predicting new iron garnet thin films with perpendicular magnetic anisotropy. *Journal of Magnetism and Magnetic Materials* 499, 166108. <https://doi.org/10.1016/j.jmmm.2019.166108>.

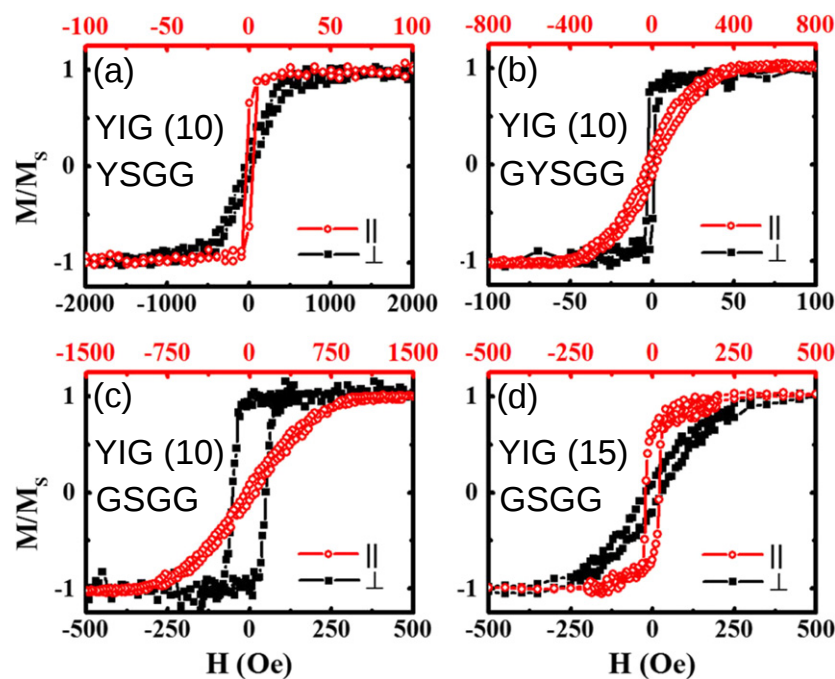


Fig. 5 In-plane (red) and out-of-plane (black) magnetic hysteresis loops of 10 nm thick YIG films grown on (a) YSGG, (b) GYSGG, (c) GSGG substrates, and (d) of a 15 nm thick YIG/GSGG sample. A tensile lattice mismatch $\varepsilon_{||} > 1\%$ is necessary to achieve PMA, as provided by film growth on GYSGG or GSGG substrates. However, for a partially relaxed 15 nm thick film on GSGG an in-plane magnetic easy axis is observed (d). The values in parenthesis denote the film thickness in nm. Reproduced with permission from Li, G., Bai, H., Su, J., *et al.*, 2019. Tunable perpendicular magnetic anisotropy in epitaxial $\text{Y}_3\text{Fe}_5\text{O}_{12}$ films. *Applied Physics Letters Materials* 7 (4), 041104. <https://doi.org/10.1063/1.5090292>, © 2019, APL.

TmIG A well-studied alternative is thulium iron garnet (TmIG) as it possesses an about twice as high λ_{111} of -5.2×10^{-6} and a slightly reduced saturation magnetization of about $111 \frac{\text{kA}}{\text{m}}$. Therefore, TmIG films exhibiting PMA have been realized on various substrates, including GGG (Wu *et al.*, 2018; Quindeau *et al.*, 2017; Vilela *et al.*, 2020; Duong *et al.*, 2022), sGGG (Ciubotariu *et al.*, 2019), and GSGG (Vilela *et al.*, 2020; Tang *et al.*, 2016). Hereby, a strain of around 0.3% for films grown on GGG substrates is sufficient to induce PMA (Wu *et al.*, 2018; Vilela *et al.*, 2020), while films experiencing more strain on sGGG or GSGG substrates show stronger PMA (Ciubotariu *et al.*, 2019; Vilela *et al.*, 2020), as expected. Additionally, strain relaxation and a corresponding reorientation transition to an in-plane magnetic easy axis were reported for films grown on sGGG thicker than 70 nm (Ciubotariu *et al.*, 2019), or for films grown on GGG thicker than 30 nm (Duong *et al.*, 2022).

EuIG In contrast, europium iron garnet (EuIG) has a positive magnetostriction constant, and a reduced M_s . Therefore, thin films grown under a large compressive strain show PMA, e.g., up to 56 nm thick Eu-rich EuIG/GGG films (Rosenberg *et al.*, 2018). However, as EuIG has an one order of magnitude larger magnetostriction constant in [001] direction, films grown on (001) oriented GGG are more popular (Rosenberg *et al.*, 2018; Ortiz *et al.*, 2018; Warren *et al.*, 2022). An extensive FMR study of EuIG thin films grown on different substrates revealed first- and second-order uniaxial anisotropy terms, showing a linear and quadratic dependence on the strain, respectively (Ortiz *et al.*, 2021a).

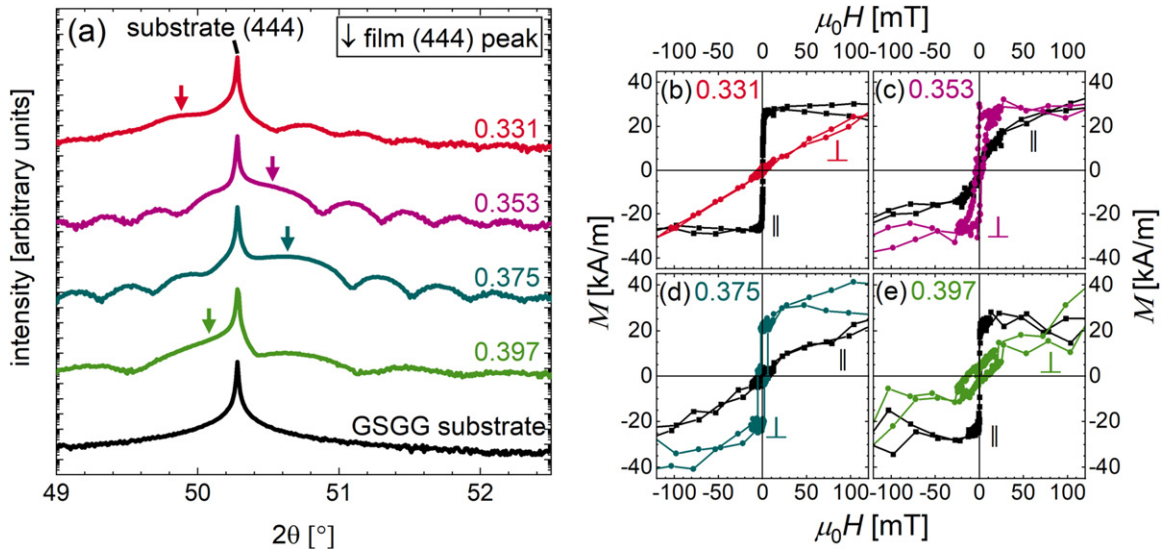


Fig. 6 (a) X-ray diffractogram of GdIG films with varying Gd/Fe composition grown on GSGG. Stoichiometric GdIG has a ratio of $\frac{\text{Gd}}{\text{Gd}+\text{Fe}} = 0.375$. (b-e) Corresponding hysteresis loops, showing a transition from an out-of-plane to an in-plane magnetic easy axis with increasing off-stoichiometry.

GdIG and DyIG Gadolinium (GdIG) and dysprosium iron garnet (DyIG) thin films have a magnetic compensation point, and therefore show a highly temperature-dependent M_s and consequently K_s . GdIG as well as DyIG thin films with $\lambda_{111} < 0$ grown under tensile in-plane strain, e.g., on GSGG substrates, show PMA at room temperature, while films grown under compressive strain, e.g., on GGG substrates, possess an in-plane magnetic easy axis (Bauer *et al.*, 2020; Holzmann *et al.*, 2022; Zhou *et al.*, 2021b; Li *et al.*, 2022b). Furthermore, GdIG/GSGG samples are reported to exhibit only little strain relaxation and to maintain PMA up to a thickness of 220 nm (Holzmann *et al.*, 2022), while already small deviations in stoichiometry lead to a change from compressive to tensile OOP strain and subsequent loss of PMA, as shown in Fig. 6. Due to the magnetic compensation point around room temperature, M_s increases strongly with decreasing temperature, and a spin reorientation transition towards an in-plane magnetic easy axis was found at around 150 K for GdIG/GSGG thin films (Holzmann *et al.*, 2022).

TbIG While terbium iron garnet (TbIG) has a similar magnetization and compensation temperature as GdIG, it has an increased positive magnetostriction constant λ_{111} of 12×10^{-6} . Therefore, compressive in-plane strain is necessary for K_{ind} to favor PMA. In this regard, TbIG/GGG samples show PMA for up to 100 nm thickness (Ortiz *et al.*, 2018; Damerio and Avci, 2023), while Tb-rich films on the same substrate were reported to remain out-of-plane up to a thickness of about 50 nm (Rosenberg *et al.*, 2018). Sc-substituted TbIG films were reported to show PMA and a reduced compensation temperature, as the Sc ions replace Fe ions at the octahedral lattice sites (Khurana *et al.*, 2021).

SmIG Samarium iron garnet (SmIG) has a high saturation magnetization, similar to YIG, but at the same time one of the largest magnetostriction constants of the iron garnets, for both (Geprägs *et al.*, 2016) and [001] directions (see Table 1). PMA was reported for SmIG/GGG(001) thin films (Yamahara *et al.*, 2021, 2011; Shen *et al.*, 2021), while a strain relaxation process promoted via the formation of dislocations was observed for film thicknesses above 40 nm (Yamahara *et al.*, 2021). Fig. 7(a) shows a high-resolution transmission electron microscope (TEM) image of a 108 nm-thick SmIG thin film revealing a single crystalline structure with the presence of a step dislocation for stress relaxation (Yamahara *et al.*, 2021).

ErIG, HoIG, and YbIG For erbium (ErIG), holmium (HoIG), and ytterbium (YbIG) iron garnets no reports on thin films exhibiting PMA are yet known to the best of our knowledge. However, thin films exhibiting tensile in-plane strain on, for example, GSGG substrates are expected to show PMA (see Fig. 4). Interestingly, μm -thick HoIG films showed a temperature-dependent, noncollinear orientation of the magnetic moments of the different sublattices (Kalashnikova *et al.*, 2012). Similarly, a sign change of the cubic magnetocrystalline anisotropy constant K_1 below 30 – 60 K, and consequently a spin reorientation transition from an (Geprägs *et al.*, 2016)- to an [001]-oriented magnetic easy axis was reported for bulk ErIG, among other garnets (Xu *et al.*, 2022; Strohm *et al.*, 2012; Guillot *et al.*, 1981; Hock *et al.*, 1991; Geller and Balestrino, 1980; Greneche and Pascard, 1995; Lahoubi *et al.*, 2009).

Bi:YIG and Ce:YIG Bi- or Ce-doped YIG films are especially popular for magneto-optical applications, as the Bi or Ce substitutions can drastically enhance the magneto-optical effect (Stadler and Mizumoto, 2014; Srinivasan and Stadler, 2022; Fakhru *et al.*, 2021; Yoshihara *et al.*, 2022). While many studies are focused on integrating such polycrystalline films on non-garnet substrates, these substitutions are also suitable to tune the magnetic anisotropy of single-crystalline YIG films, showing low magnetic losses and only a small increase in spin wave damping compared to other rare earth substitutions (Soumah *et al.*, 2018). On the one hand, Bi- or Ce:YIG films typically possess a larger magnetostriction constant than pure YIG, increasing the magnetoelastic anisotropy. On the other hand, the presence of different ions on the dodecahedral lattice sites promotes an additional growth-induced anisotropy. For example, $\text{Bi}^{1/2}\text{Fe}^{5/2}\text{O}^{12}$ thin films exhibiting PMA were realized on sGGG (Soumah *et al.*, 2018; Evelt *et al.*, 2018) and GSGG substrates (Zhang *et al.*, 2021), revealing a low damping of 3×10^{-4} (Soumah *et al.*, 2018). Moreover, a strong decrease of the

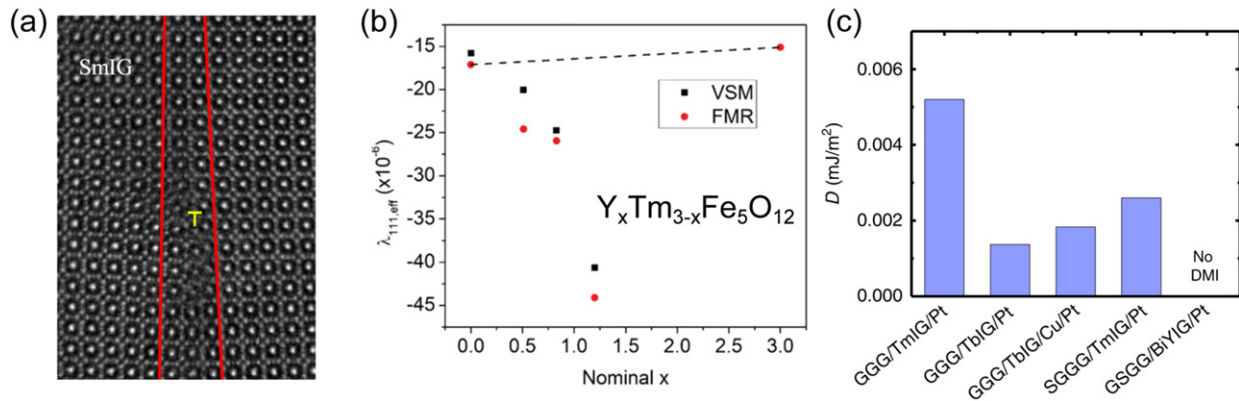


Fig. 7 (a) TEM image of a 108 nm thick SmIG film, showing stress relaxation via the formation of step dislocations. (b) Effective magnetostriction constant λ_{111} in dependence of the nominal Y content x in $Y_xTm_{3-x}Fe_5O_{12}$. (c) DMI strength depending on the rare-earth element, the metallic top layer, and substrate induced strain. (a) Reproduced under a Creative Commons Attribution 4.0 license (Creative Commons. Attribution 4.0 International License. 2013. Available at: <https://creativecommons.org/licenses/by/4.0/>) from Yamahara, H., Feng, B., Seki, M., *et al.*, 2021. Flexoelectric nanodomains in rare-earth iron garnet thin films under strain gradient, *Communications Materials* 2, 95. <https://doi.org/10.1038/s43246-021-00199-y>, © 2021, Springer Nature. (b) Reproduced with permission from Rosenberg, E.R., Litzius, K., Shaw, J.M., *et al.*, 2021. Magnetic properties and growth-induced anisotropy in yttrium thulium iron garnet thin films. *Advanced Electronic Materials* 7, 2100452. <https://doi.org/10.1002/aem.202100452>, © 2021, WILEY VCH. (c) Reproduced under a Creative Commons Attribution 4.0 license (Creative Commons. Attribution 4.0 International License. 2013. Available at: <https://creativecommons.org/licenses/by/4.0/>) from Caretta, L., Rosenberg, E., Büttner, F., *et al.*, 2020a. Interfacial Dzyaloshinskii-Moriya interaction arising from rare-earth orbital magnetism in insulating magnetic oxides, *Nature Communications* 11, 1090. <https://doi.org/10.1038/s41467-020-14924-7>, © 2020, Springer Nature.

growth-induced anisotropy with increasing growth temperature was found in Bi:YIG films (Gouéré *et al.*, 2022). Similarly, Ce:YIG films were grown on GGG substrates with various orientations, showing an in-plane magnetic easy axis (Onbasli *et al.*, 2016). While pure BiIG or CeIG are not a-priori stable in bulk form, epitaxially grown BiIG thin films were realized on GGG substrates, showing PMA for ultra-thin films (Popova *et al.*, 2012, 2013), and additionally, an enhanced magnetoelectric effect (Popova *et al.*, 2017).

Polycrystalline films This situation is different for polycrystalline REIG thin films. Typically these films do not even show a preferred texture. In this case, the average magnetostriction constant is given by a weighted average of the magnetostriction constants along the main axes $\lambda = \frac{2}{5}\lambda_{001} + \frac{3}{5}\lambda_{111}$ (Bauer *et al.*, 2020, 2019). Due to the different thermal expansion of film and substrate, a lattice mismatch $\varepsilon = \Delta\alpha\Delta T$ develops, given by the difference in the thermal expansion coefficient $\Delta\alpha = \alpha_{\text{sub}} - \alpha_{\text{film}}$ and the temperature difference during cooling ΔT (Bauer *et al.*, 2020, 2019). In the case of Si substrates, α_{sub} (3×10^{-6} 1/K (Okada and Tokumaru, 1984)) is smaller than α_{film} (about 2×10^{-5} 1/K (Geller *et al.*, 1969)), and therefore tensile strain is expected. Consequently, garnets with overall negative magnetostriction constant λ are expected to favor PMA when grown on Si substrates. It has been shown that DyIG/Si films show PMA (Bauer *et al.*, 2020), with both $\lambda_{111} < 0$ and $\lambda_{001} < 0$, while EuIG/Si films have an in-plane magnetic easy axis (Bauer *et al.*, 2019), as both $\lambda_{111} > 0$ and $\lambda_{001} > 0$. However, in both cases cracks in the thin films appear due to the difference in thermal expansion coefficients, as demonstrated in Fig. 3 for DyIG (Bauer *et al.*, 2020).

As shown in the examples above, in-plane tensile (compressive) strain leads to a magnetoelastic anisotropy favoring PMA for single-crystalline films with a negative (positive) magnetostriction constant. Consequently, highly strained ultra-thin films show PMA, but for thicker films typically strain relaxation and a subsequent decrease in magnetoelastic anisotropy lead to a transition from an out-of-plane to an in-plane magnetic easy axis. In most cases, strongly strained films show a fast relaxation within a few 10 nm, while weakly strained films can maintain the strained state up to a thickness of some 100 nm (Ortiz *et al.*, 2018; Fu *et al.*, 2017). While strain relaxation via dislocations was shown for SmIG thin films (Fig. 7(a)) (Yamahara *et al.*, 2021), no such studies are yet known for other garnets.

Furthermore, epitaxially grown garnet films tolerate a sizeable off-stoichiometry. By intentionally growing off-stoichiometric thin films, the elastic and magnetic properties can be further tailored. While off-stoichiometric film growth can have multiple effects including the formation of RE^{2+} or RE^{4+} ions (Rosenberg *et al.*, 2018) as well as oxygen vacancies (Swamy *et al.*, 2021), the strain-state of the thin films is strongly dependent on the film composition as well. For TmIG/GGG(111) films, an enhancement of the PMA was reported, caused by an increased strain of Tm-rich films (Wu *et al.*, 2018), while for TbIG/GGG(111) films increased PMA was found for Tb-deficient films. (Damerio and Avcı, 2023) Contrary, GdIG/GSGG(111) (Holzmann *et al.*, 2022) and EuIG/GGG(001) samples (Guo *et al.*, 2022) showed a decrease in strain and reduction in PMA with increasing off-stoichiometry, ultimately leading to a loss in PMA, as shown in Fig. 6.

The growth-induced anisotropy K_G in mixed garnets offers another way to alter the magnetic anisotropy, independent of the used substrate. It relies on the preferential ordering of different ions on unequal crystallographic sites during the growth process (Gyorgy *et al.*, 1973; Callen, 1971), and was already discovered in LPE-grown films for bubble memory devices in the 1970s (Boback *et al.*, 1970). It was shown that post-deposition annealing can revoke this ordering, as K_g decreases with increasing annealing time (Hagedorn, 1974). More recently, the growth-induced anisotropy in PLD-grown $Y_xTm_{3-x}Fe_5O_{12}$ (YTmIG) thin films was studied (Rosenberg *et al.*, 2021; Bai *et al.*, 2022). It was shown that PMA cannot be explained solely by magnetoelastic anisotropy, but a growth-induced contribution K_G is necessary, which is proportional to the yttrium content x as $K_G \propto x(3-x)^2$ (Rosenberg *et al.*, 2021) and maximized for a 1:1 mixture of Y and Tm. Fig. 7(b) shows the effective magnetostriction constant λ_{111} in dependence of

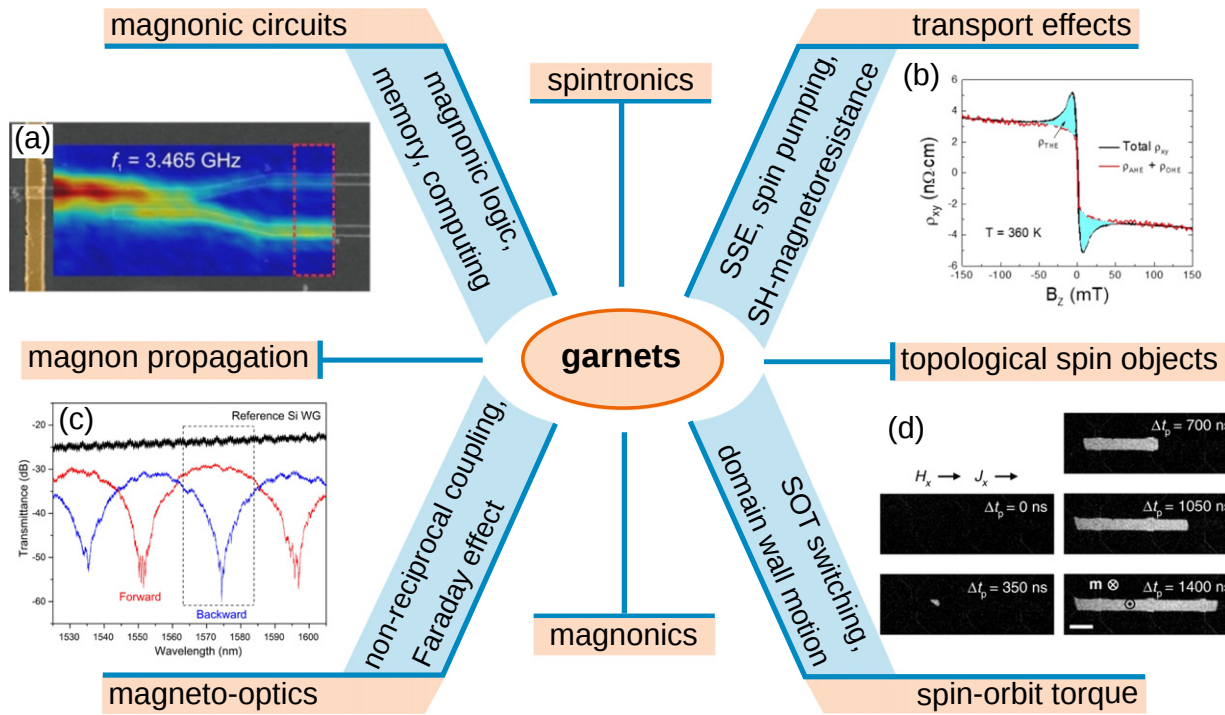


Fig. 8 Selected research fields and applications of iron garnet thin films. (a) Magnon intensity as recorded by Brillouin light scattering in a prototype of a magnonic directional coupler, consisting of two YIG wave guides. (b) Hall resistivity ρ_{xy} of a TmIG(3.2 nm)/Pt(5 nm) bilayer with contributions from the ordinary, anomalous, and topological Hall effect. (c) Non-reciprocity of the forward and backward optical modes in a Si-based Mach-Zehnder interferometer utilizing the transverse magnetic mode of a Ce:YIG magneto-optical film, magnetized in a field of 100 mT. (d) Domain wall motion in a TmIG(8.3 nm)/Pt(5 nm) racetrack (width 10 μ m) induced by a driving current J_x of 0.65^8 A/m $^{-2}$ with pulse length 350 ns as well as an applied magnetic field $H_x = 250$ Oe, recorded by Kerr microscopy. (a) Reproduced with permission from Wang, Q., Kewenig, M., Schneider, M., *et al.*, 2020. A magnonic directional coupler for integrated magnonic half-adders. *Nature Electronics* 3, 765. <https://doi.org/10.1038/s41928-020-00485-6>, © 2020, Springer Nature. (b) Shao, Q., Liu, Y., Yu, G., *et al.*, 2019b. Topological Hall effect at above room temperature in heterostructures composed of a magnetic insulator and a heavy metal. *Nature Electronics* 2, 182. <https://doi.org/10.1038/s41928-019-0246-x>, © 2019, Springer Nature. (c) Zhang, Y., Du, Q., Wang, C., *et al.*, 2019a. Monolithic integration of broadband optical isolators for polarization-diverse silicon photonics, *Optica* 6 (4), 473. doi: 10.1364/OPTICA.6.000473, © 2019, The Optical Society. (d) Reproduced under a Creative Commons Attribution 4.0 license (Creative Commons. Attribution 4.0 International License. 2013 Available at: <https://creativecommons.org/licenses/by/4.0/>) from Vélez, S., Schaab, J., Wörmle, M., *et al.*, 2019. High-speed domain wall racetracks in a magnetic insulator. *Nature Communications* 10, 4750. <https://doi.org/10.1038/s41467-019-12676-7>, © 2019, Springer Nature.

the nominal Y content x , clearly revealing an increased λ_{111} , deviating from a linear behavior between YIG and TmIG, suggesting an additional source of anisotropy (Rosenberg *et al.*, 2021). Similarly, a growth-induced anisotropy should appear for Fe substitutions on the octahedral or tetrahedral sites (Manuilov *et al.*, 2009), or induced by off-stoichiometric growth, e.g., ordering of Fe $^{2+}$ impurities at temperatures below 175 °C is suspected to cause a spin reorientation transition in YIG (Sankar *et al.*, 2017). Additionally, studies on Bi:YIG films showed a strong decrease of K_G with increasing garnet growth temperature (Gouéré *et al.*, 2022).

While for LPE-grown garnets a difference in ion radii Δ of at least 5 pm between the different ion species was suspected to be necessary for K_G to have a measurable effect (Eschenfelder, 2012), this condition seems not to hold for YtMIG ($\Delta < 4$ pm), probably due to the highly non-equilibrium PLD growth process (Rosenberg *et al.*, 2021).

While so far only single garnet layers were considered, garnet/garnet or garnet/metal heterostructures offer a diverse platform for magnonic and spintronic research. Garnet thin films in proximity to a heavy metal layer like Pt or W are especially interesting to study interface-induced effects. Hereby, chiral domain walls and skyrmions in garnet thin films were recently observed (Avci *et al.*, 2019; Vélez *et al.*, 2019; Büttner *et al.*, 2020; Vélez *et al.*, 2022). Similar to metallic interfaces, the symmetry breaking at the film interfaces causes an interfacial Dzyaloshinskii-Moriya interaction (iDMI) in the insulating garnets, which can stabilize these spin textures. However, the origin of the iDMI in such insulating films is more complex (Caretta *et al.*, 2020a; Ding *et al.*, 2020b, 2019; Xia *et al.*, 2022; Lee *et al.*, 2020a,b; Ye *et al.*, 2022). It was shown that the main cause for iDMI in garnet thin films is the orbital momentum and spin-orbit coupling of the RE ions themselves, originating at both the garnet/metal and garnet/substrate interface (Caretta *et al.*, 2020a; Ding *et al.*, 2020b, 2019; Fakhruel *et al.*, 2023). Consequently, the strength of the iDMI is strongly influenced by the RE element choice, the strain in the film, as well as the temperature, but interestingly to a less extent by the selected heavy metal (Caretta *et al.*, 2020a; Xia *et al.*, 2022). Fig. 7(c) highlights the strong effect of the RE choice on the DMI constant, but shows only a small change, when inserting a Cu spacer layer between garnet and heavy metal (Caretta *et al.*, 2020a). However, contrary

reports find a strong dependence of the iDMI on the heavy metal layer (Lee *et al.*, 2020a,b), and a competition between substrate and metal interface induced iDMI was proposed (Vélez *et al.*, 2019).

Finally, multilayers consisting of different garnets provide the possibility to further tune the magnetic properties. It was reported that in YIG/GdIG bilayers, the iron sublattices of YIG and GdIG couple ferromagnetically, which causes a temperature and field-dependent (anti-) ferromagnetic alignment of the total magnetization of the YIG and the GdIG layer (Becker *et al.*, 2021; Gomez-Perez *et al.*, 2018; Roos *et al.*, 2022), offering a potential pathway to efficiently manipulate, for instance, magnon transport (Yan *et al.*, 2021; Li *et al.*, 2020).

Applications in Magnonics and Spintronics

Iron garnets with their insulating and ferrimagnetic nature provide a variety of unique properties including a high Néel temperature, ultra-low spin wave damping, and strong magneto-optical coupling, which allow studying a wide range of fundamental effects. Additionally, their stability against heat, oxidation, and aging makes them further interesting for applications. Fig. 8 illustrates selected research areas where garnet thin films are commonly utilized. In the following, an overview with focus on the spin Seebeck effect in compensated garnets is given, while for more comprehensive information the reader is referred to the respective literature given in the text.

The ultra-low damping of garnet thin films makes them the preferred material to study magnons, typically propagating at GHz to THz frequencies. Hereby, fundamental research on the excitation, propagation, and manipulation of spin waves is performed, as well as moving forward into potential applications, e.g., in magnonic-based neuromorphic computing, magnonic logic valves or memory. More recently, also quantum magnonics including Bose-Einstein condensates (Serga *et al.*, 2010; Pirro *et al.*, 2021; Barman *et al.*, 2021; Mahmoud *et al.*, 2020; Sheng *et al.*, 2021; Chumak *et al.*, 2022; Rana and Otani, 2019; Demokritov *et al.*, 2006) and 2D magnonics (Wei *et al.*, 2022; Mendes *et al.*, 2015; Wang *et al.*, 2022) gained attention. A prototype of a magnonic logic unit, a directional coupler, is shown in Fig. 8(a). It consists of two 350 nm wide YIG waveguides, separated by a 320 nm gap (Wang *et al.*, 2020). In the linear regime, the dipolar interaction between the waveguides splits the dispersion relation of an incoming magnon in a symmetric and an antisymmetric mode, which causes an oscillation between the two waveguides. Depending on the frequency (and length of the waveguide), the magnon ends up in one of them. In the non-linear regime, the waveguide selection can be additionally controlled by the microwave power of the excitation strip. Despite prototypes that have proven the concept of magnonic computing, no all-magnonic computing units are commercially available yet.

On the other hand, bilayers consisting of garnets and heavy metals like Pt are widely studied in the field of spintronics, including a range of transport effects like spin pumping, spin Seebeck effect, or spin Hall magnetoresistance (Dieny *et al.*, 2020; Yang *et al.*, 2021a; Avci, 2021; Fulara *et al.*, 2019; Demidov *et al.*, 2020; Uchida *et al.*, 2008, 2010a; Li *et al.*, 2022b; Nakayama *et al.*, 2013). In Fig. 8(b), the field-dependent Hall resistivity ρ_{xy} of a TmIG(3.2 nm)/Pt(5 nm) bilayer reveals contributions from the ordinary and anomalous Hall effect, but also the signature of the topological Hall effect, shaded in blue, which hints at the presence of topologically protected spin objects (Shao *et al.*, 2019b). Indeed, bubble skyrmions were already observed in such garnet bilayers (Büttner *et al.*, 2020; Vélez *et al.*, 2022). Furthermore, the ferrimagnetic nature with a magnetic compensation point allows the study of (quasi) antiferromagnetic spintronics as well (Kim *et al.*, 2022; Zhou *et al.*, 2021a).

Moreover, the magneto-optical coupling of the garnets drives research into the integration of garnets into photonic devices. While the growth of high-quality garnet films on Si remains challenging, first prototypes are promising (Srinivasan and Stadler, 2022). Fig. 8(c) shows the transmission spectrum of a Mach-Zehnder interferometer in conjunction with a Ce:YIG layer (Zhang *et al.*, 2019a). In an applied field of 100 mT, the transverse magnetic mode isolator shows a maximum isolation ratio of 30 dB between forward and backward propagating modes, phase shifted by π , and an insertion loss of 5 dB. This offers comparable performance to traditional bulk devices, but at a lower footprint. In addition, the magneto-optical properties of garnets are also studied in light-induced magnonics (Soumah *et al.*, 2021; Zeuschner *et al.*, 2022; Deb *et al.*, 2022) and all-optical switching of garnets (Stupakiewicz and Satoh, 2021; Frej *et al.*, 2021; Stupakiewicz *et al.*, 2021, 2017; Kimel *et al.*, 2009, 2004).

A spin-polarized current in a metal layer adjacent to an insulating garnet naturally exerts a spin-orbit torque (SOT) on the magnetic moments of the garnet, which gives rise to an energy-efficient and fast way to manipulate the garnet's magnetization. Next to the before discussed transport phenomena, SOT-induced domain wall motion and eventually magnetization switching are widely studied (Avci, 2021; Fulara *et al.*, 2019; Demidov *et al.*, 2020; Li *et al.*, 2022b; Avci *et al.*, 2019; Caretta *et al.*, 2020b). Fig. 8(d) shows the SOT-driven propagation of a Néel domain wall in a TmIG/Pt racetrack (Vélez *et al.*, 2019). Notably, the garnets were found to possess ultra-fast moving domain walls. It was shown that the domain wall speed approaches a limit of about $4300 \frac{\text{m}}{\text{s}}$ in Bi:YIG(6.9 nm)/Pt(4 nm) films without an applied out-of-plane field, which was attributed to magnetic solitons moving at about 10% of the relativistic limit (Caretta *et al.*, 2020b).

At last, the spin Seebeck effect (SSE) is a promising way to develop new thermoelectric devices, but can also act as a source of pure spin currents (magnons). It is the magnetic analogon to the conventional Seebeck effect and describes the conversion of a heat gradient ∇T to a spin current I_s , where one distinguishes between the longitudinal ($\nabla T \parallel I_s$, LSSE) and the transverse ($\nabla T \perp I_s$, TSSE) geometry (Uchida *et al.*, 2014). It was first discovered in 2008 in metals (Uchida *et al.*, 2008), and shortly afterward in 2010 in magnetic insulators, namely in YIG and LaYIG (Uchida *et al.*, 2010a, 2010b). The inverse effect, converting a spin current into a heat current, is the spin Peltier effect (Yagmur *et al.*, 2018).

In contrast to the conventional Seebeck effect, the SSE scales with the area perpendicular to the heat gradient, and the SSE material can be separated from any conducting layers. This makes bilayers of magnetic insulators and conducting metals a promising candidate for thermoelectric power generation, as the generated spin current is converted into a charge current in the metal layer by the inverse spin Hall effect (Uchida *et al.*, 2014; Shi *et al.*, 2020; Kirihaara *et al.*, 2012, 2016). Furthermore, the SSE in insulators like garnets can generate a pure spin current, reaching magnon propagation lengths in the order of 100 nm (Kehlberger *et al.*, 2015; Chanda *et al.*, 2022b).

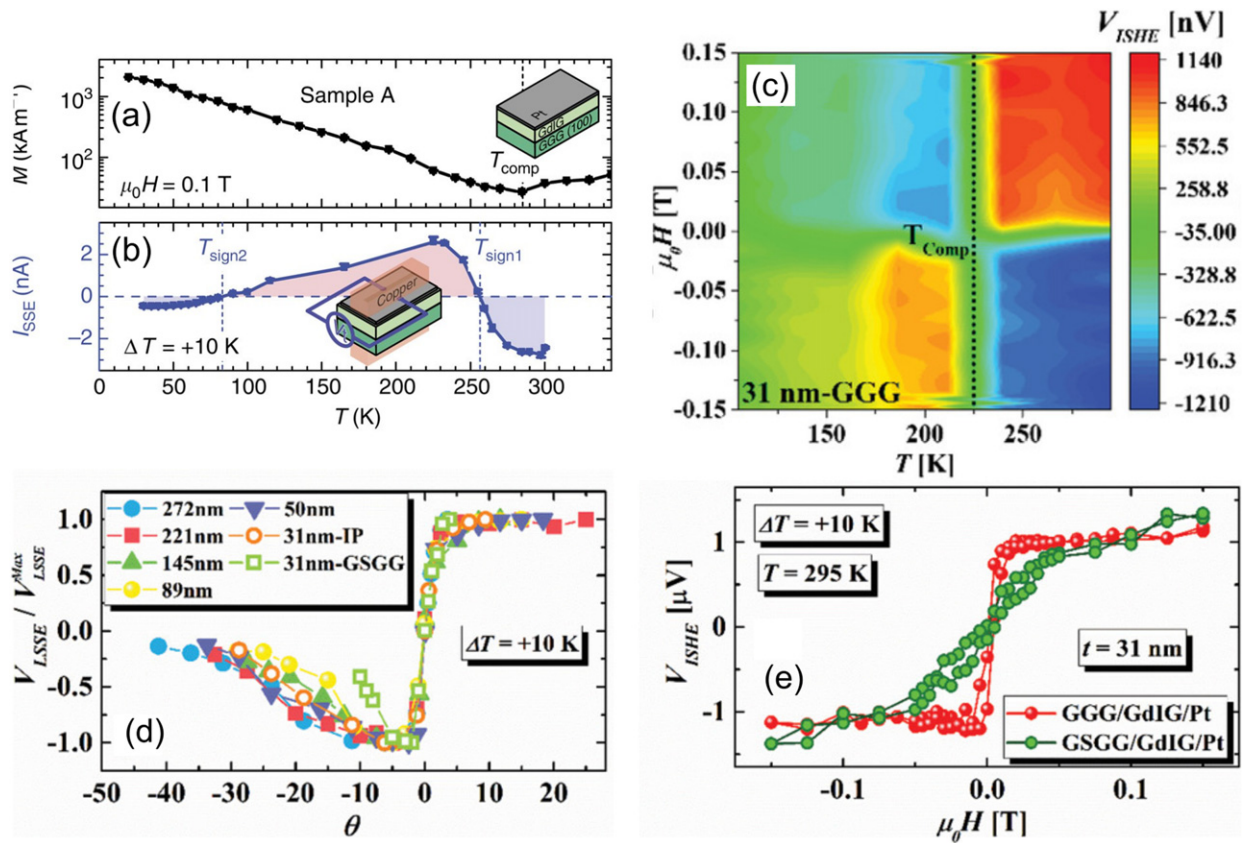


Fig. 9 Temperature dependence of (a) the magnetization M and (b) the spin Seebeck current I_{SSE} for a 100 nm thick GdIG film grown on GGG. (c) H - T phase map for a 100 nm thick GdIG film grown on GGG, showing the spin Seebeck voltage V_{LSSE} . (d) Normalized temperature dependence of V_{LSSE} for films with different thicknesses and (e) field-dependent V_{LSSE} signal for GdIG film grown on GGG and GSGG substrates, showing an in-plane easy and hard axis loop, respectively. (a–b) Reproduced under a Creative Commons Attribution 4.0 license (Creative Commons Attribution 4.0 International License, 2013. Available at: <https://creativecommons.org/licenses/by/4.0/>) from Geprägs, S., Kehlberger, A., Coletta, F.D., *et al.*, 2016. Origin of the spin Seebeck effect in compensated ferrimagnets. *Nature Communications* 7, 10452. <https://doi.org/10.1038/ncomms10452>, © 2016, Springer Nature. (c–e) Reproduced with permission from Chanda, A., Holzmann, C., Schulz, N., *et al.*, 2022a. Scaling of the thermally induced sign inversion of longitudinal spin Seebeck effect in a compensated ferrimagnet: Role of magnetic anisotropy. *Advanced Functional Materials* 32 (9), 2109170. <https://doi.org/10.1002/adfm.202109170>, © 2022, WILEY VCH.

While early on research was focused on YIG (Uchida *et al.*, 2010b; Kehlberger *et al.*, 2015; Weiler *et al.*, 2012), compensated rare-earth garnets have recently attracted great attention (Geprägs *et al.*, 2016; Chanda *et al.*, 2022a,b; Cramer *et al.*, 2017; Ortiz *et al.*, 2021b; Yang *et al.*, 2021b). It was observed that the SSE voltage $V_{(L)SSE}$ (or the SSE current $I_{(L)SSE}$) changes sign twice in a GdIG thin film, when decreasing the temperature (Fig. 9(a–b)). While the first sign change is attributed to the magnetic compensation point of GdIG, the second sign change at a lower temperature is explained by the interplay of a gapped and a gapless magnon mode in combination with their conversion to a charge current at the Pt interface (Geprägs *et al.*, 2016). Furthermore, the sign reversal of $V_{(L)SSE}$ is observed for different compensated garnets and different metal layers (Cramer *et al.*, 2017), as well as independent of the film thickness, the position of the compensation temperature, or the magnetic anisotropy, as shown in Fig. 9(d) (Chanda *et al.*, 2022a). On the other hand, field-dependent measurements of $V_{(L)SSE}$ show a clear dependence on the magnetic anisotropy (Fig. 9(e)) (Chanda *et al.*, 2022a). Therefore, the SSE gives insight into the magnetic anisotropy, the magnetic ordering, and the magnon population, as well as their coupling at the garnet/metal interface (Kikkawa and Saitoh, 2023), enabling the design of potential new thermoelectric devices (Shi *et al.*, 2020).

Conclusion

Rare earth iron garnets (REIGs) are a fascinating material with unique magnetic properties. Nowadays, significant advances in thin film growth and processing make the REIGs a versatile materials system. In particular, the ferrimagnetic and insulating nature of the REIGs combined with ultra-low spin wave damping offers an ideal platform to study the excitation, propagation, manipulation, and

interaction of spin waves. Furthermore, RE substitutions, strain- or stoichiometry induced effects, varying film thicknesses, or multilayers of different garnet stacks offer a rich tunability of their magnetic properties. This includes, for example, the control of the spin wave damping and spectrum, the magnetic anisotropy, and the magnetic compensation point. Therefore, REIGs are employed for a variety of fundamental studies, including spin-wave computing, spin-orbit torques, magneto-optical effects, and the spin Seebeck effect. Their diverse properties will ensure their status as the go-to material for fundamental research on spintronics and magnonics, however, due to their demanding growth process, integration in applications remains a challenge to be solved.

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Helimagnetism: Fundamental Physics and Applications to Electronics

David Mandrus, University of Tennessee, Knoxville, TN, United States and Oak Ridge National Laboratory, Oak Ridge, TN, United States

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Abstract

In this article the basic properties of Yoshimori-type and Dzyaloshinskii-type helimagnets are reviewed, followed by a discussion of several electronic functionalities of helimagnets that have been investigated in recent years. These include some interesting properties of a monoaxial chiral helimagnet, most notably realized in CrNb_3S_6 , that include a magnetically tunable periodicity, 1D magnetic solitons, and a huge electrical magnetochiral effect. Other electronic functionalities discussed include the ability of helimagnets to create miniature inductors, and the possibility of controlling the handedness of helimagnets in order to encode information.

Key Points

- There are two types of helimagnets, Yoshimori-type and Dzyaloshinskii-type.
- Yoshimori-type helimagnets have both left- and right- handed spirals, whereas Dzyaloshinskii-type have just one handedness.
- Magnetic solitons appear in a monoaxial chiral helimagnet under modest applied fields.
- Helimagnets can have a large electrical magnetochiral effect.
- Helimagnets are a promising path toward miniaturizing inductors.
- The chiral degree of freedom in a Yoshimori-type helimagnet can be controlled and can in principle be used to encode information.

Introduction

The magnetic properties of a solid are determined by billions of microscopic magnets called spins, and these spins can arrange themselves into patterns that define the type of magnetic order in a solid. For example, if the spins are all aligned in the same direction, the material is known as a ferromagnet, and if nearby spins are aligned oppositely the material is known as an antiferromagnet. Many more complex types of spin order can exist as well. These complex types of spin order profoundly affect the motion of the itinerant electrons in the material, and in some cases can give rise to new electronic functionalities. A good entry point into these effects is the phenomenon of helical magnetic order, which is the subject of this article. In a helimagnet, the spins are arranged in chains and the spin direction rotates around the axis of the helix. Usually, the helical order is determined by a delicate balance between competing magnetic interactions and magnetic anisotropies, and this balance can easily be upset by modest magnetic fields and even electrical current. It is the response of the helimagnet to magnetic fields and electrical currents that leads to new phenomena. In this article, we will first discuss the fundamentals of helimagnetism, and then discuss some of the new phenomena discovered in recent years that is relevant to electronics.

Fundamentals

Helimagnetism is a type of magnetic order in which the local magnetization rotates smoothly in a plane perpendicular to a helical axis as one moves along the axis. A simple example is provided by a layer structure in which the magnetic moments in each layer are oriented ferromagnetically and parallel to the layer, and that as one moves from layer-to-layer the direction of the moments changes by θ , known as the pitch angle. Such a situation is illustrated in [Fig. 1](#). The theory of such systems was first worked out by Yoshimori in 1959, stimulated by neutron diffraction data on MnO_2 ([Yoshimori, 1959](#)).

Let the interaction between moments in neighboring layers be given by J_1 and the interaction between next nearest layers be given by J_2 . Starting from the Hamiltonian:

$$\hat{\mathcal{H}} = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j,$$

the energy of the system can be written:

$$E = -NS^2J_1\cos\theta - NS^2J_1\cos - \theta - NS^2J_2\cos 2\theta - NS^2J_2\cos - 2\theta,$$

where N is the number of moments in each layer.

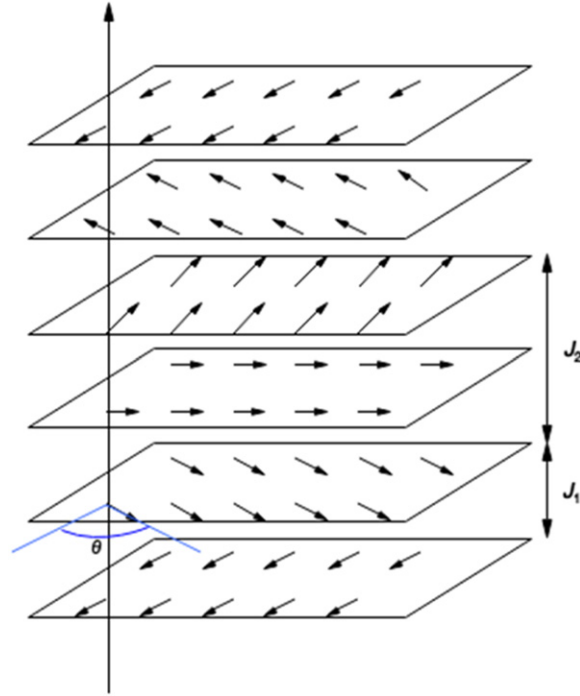


Fig. 1 Yoshimori-type helical ordering. The spins rotate by the pitch angle θ from one layer to the next. J_1 is the interaction between nearest neighbor layers. J_2 is the interaction between next nearest layer neighbors.

Simplifying, we have:

$$E = -2NS^2(J_1\cos\theta + J_2\cos 2\theta).$$

Setting $\partial E/\partial\theta = 0$, we find that the energy is minimized when:

$$(J_1 + 4J_2\cos\theta)\sin\theta = 0.$$

This yields two solutions: (1) $\sin\theta = 0$, implying that $\theta = 0$ (ferromagnetism) or $\theta = \pi$ (antiferromagnetism), or (2)

$$\cos\theta = -\frac{J_1}{4J_2},$$

corresponding to helical order with pitch angle θ . Helical order is favored over either ferromagnetism or antiferromagnetism when $J_2 < 0$ and $J_1 < 4J_2$ (Blundell, 2001). Note that the pitch (or period) of the helix is unrelated to the lattice structure of the material; it is an *incommensurate* modulation and represents an emergent new length scale in the system.

Yoshimori-type helical ordering is found in many materials, but most famously in the heavy rare earths Tb, Dy, and Ho. These elements crystallize in a hexagonal close-packed structure and the moments rotate in the close-packed planes with the helical axis perpendicular to the planes. In the case of the rare earths, the nearest neighbor exchange is ferromagnetic, and the second- and third- neighbor interactions are antiferromagnetic. These interactions are understood as being due to Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions mediated by the conduction electrons (Kasuya, 1956; Ruderman and Kittel, 1954; Yosida, 1957). RKKY interactions are long-ranged and change sign with distance. Other materials display helical ordering with frustrated superexchange interactions between localized spins.

Another class of helimagnets was postulated by Dzyaloshinskii (1964). In this case helical order is stabilized by the anisotropic Dzyaloshinskii–Moriya interaction (DMI) (Dzyaloshinsky, 1958; Moriya, 1960). The DMI is due to relativistic spin-orbit effects and is only allowed between moments that have no center of inversion between them. The DMI takes the form:

$$\mathcal{H}_{\text{DM}} = \mathbf{D} \cdot \mathbf{S}_1 \times \mathbf{S}_2,$$

where $\mathbf{D}$ is vector known as the Dzyaloshinskii vector when applied to the whole crystal, or the Dzyaloshinskii–Moriya vector when applied to a given pair of atoms (Khomskii, 2014). The direction of the Dzyaloshinskii–Moriya vector between two moments is given by rules formulated by Moriya (Moriya, 1960). The DMI favors perpendicular orientation of spins, and even though the magnitude of the DMI is small it can have profound effects on the magnetic properties of a material. For example, the DMI causes weak ferromagnetism in materials such as MnCO_3 and CoCO_3 . In materials with a strong ferromagnetic exchange and a much weaker antisymmetric exchange the combined effect is to twist the magnetization into a helix with a periodicity that can be tens of nanometers long and is incommensurate with the underlying lattice. For example, in the B20 material MnSi, the pitch of the helix is about 175 Å and the lattice parameter is 4.55 Å.

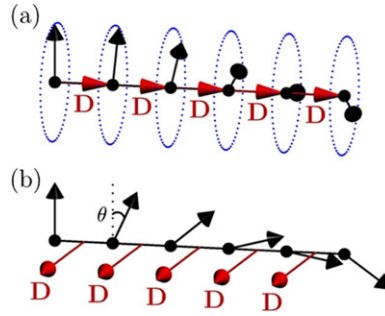


Fig. 2 The Dzyaloshinskii-Moriya interaction favors perpendicular orientation of the spins. (a) A helical magnet is formed when the Dzyaloshinskii-Moriya vector is parallel to the line connecting the spins. (b) A cycloidal magnet is formed when the Dzyaloshinskii-Moriya vector is perpendicular to the line connecting the spins.

A simple model of a Dzyaloshinskii-type helimagnet is shown in Fig. 2. Here J is the ferromagnetic exchange and D is the Dzyaloshinskii-Moriya vector coupling two moments. As shown in Fig. 2, D is parallel to the line connecting the moments in the helimagnetic case, and perpendicular to the line connecting the moments in the cycloidal case. The magnitude of the antisymmetric exchange is given by $D = D$. The wavevector and pitch of the helix is given by: $Q_0 = (1/a_0)\tan^{-1}(D/J)$ and $\text{Pitch} = 2\pi/Q_0$, where a_0 is the spacing between the moments. Typically, $D/J \approx 0.01$. The term “spiral magnet” is often used to describe helical, cycloidal, and other related forms of magnetic order.

A big difference between Yoshimori-type and Dzyaloshinskii-type helical magnets is that Dzyaloshinskii-type helical magnets are chiral (right-handed or left-handed) whereas Yoshimori-type helimagnets are expected to form domains of both right- and left-handed helices with equal probability.

Applications to Electronics

Helical, and spiral magnets more generally, display intriguing functionalities that are of potential interest for electronics. Here we will briefly review some of the emerging areas with a focus on pure helimagnets.

Monoaxial Chiral Helimagnet

The direction of the Dzyaloshinskii vector, D , determines whether the helix is right-handed or left-handed. In some materials such as MnSi there are a few symmetry-equivalent Dzyaloshinskii vectors, but in a handful of materials there is only a single Dzyaloshinskii vector. The most heavily studied of these materials is CrNb₃S₆, which is sometimes written Cr_{1/3}NbS₂ to emphasize that the compound can be thought of as the transition metal dichalcogenide NbS₂ with Cr intercalated between the layers. In CrNb₃S₆, the magnetic moments of the Cr ions order at around 130 K with the moments parallel to the NbS₂ layers, and all the moments in the same layer are ordered ferromagnetically. The Dzyaloshinskii vector points along the c -axis, so the magnetization twists into a helix with a long period of 48 nm (Miyadai *et al.*, 1983). A key feature of CrNb₃S₆ is that the 2D magnetic layers are weakly coupled along the c -axis, meaning that the system can be treated as a classical 1D system (Kishine and Ovchinnikov, 2015).

In 2012, Togawa, *et al.* showed using Lorenz microscopy that the magnetic structure of CrNb₃S₆ evolves from a helimagnet to a chiral magnetic soliton lattice when a relatively small magnetic field is applied perpendicular to the c -axis (Togawa *et al.*, 2012). As shown in Fig. 3, when a magnetic field is applied the helimagnet responds by forming forced ferromagnetic regions separated by solitons (360° domain walls). Strikingly, a new periodicity $L(H)$ appears in the system that can be tuned with a magnetic field.

Remarkably, this behavior is well-described by the 1D chiral sine-Gordon model (Kishine *et al.*, 2005), which predicts the behavior of $L(H)$ and is found to be in good agreement with experiment.

Extensive experimental and theoretical work has been performed over the past decade to understand CrNb₃S₆ and related materials. The theory has been extensively reviewed by Kishine and Ovchinnikov (Kishine and Ovchinnikov, 2015) and the experimental situation has been reviewed by Cao *et al.* (Cao *et al.*, 2020). In terms of applications to electronics, we will first discuss the manipulation of magnetic solitons, which could potentially have applications as memory devices, and then discuss the electrical magnetochiral effect.

Magnetic solitons are attractive platforms for memory devices as they are discrete, countable, and stable. One dimensional magnetic solitons were first discussed in 1964 (Dzyaloshinskii, 1964), but the first experimental realization was in CrNb₃S₆ in 2012 (Togawa *et al.*, 2012).

The soliton winding number for a 1D spin chain is given by

$$w = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \partial_x \phi,$$

where ϕ is the azimuthal angle of the spins. This winding number simply counts the number twists in the chain (Braun, 2012). A couple of studies have appeared in which individual solitons have been observed to move in and out of a small sample

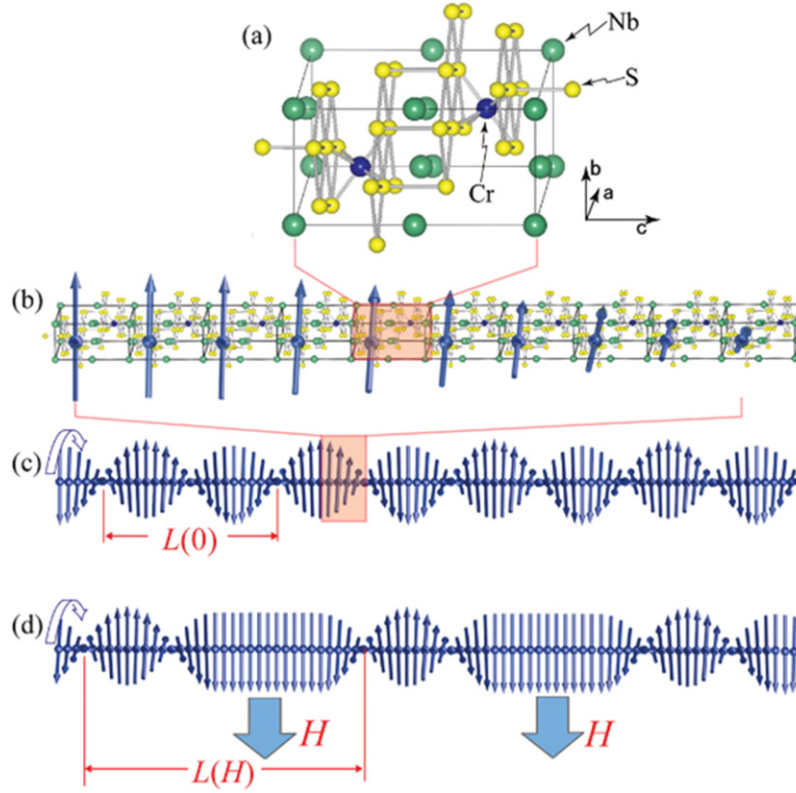


Fig. 3 (a) Unit cell of CrNb₃S₆. The Dzyaloshinskii-Moriya vectors between Cr ions in two different layers sum to a single Dzyaloshinskii vector pointing along *c* (Volkova and Marinin, 2014). (b) The magnetization in each layer rotates as one moves along *c*. (c) Zero-field helimagnetic structure. (d) Formation of a chiral magnetic soliton lattice as a magnetic field is applied perpendicular to the helical axis showing the emergence of a new length scale *L*(*H*) in the system. Reproduced with permission from Togawa, Y., Koyama, T., Takayanagi, K., *et al.*, 2012. Chiral magnetic soliton lattice on a chiral helimagnet. Phys. Rev. Lett. 108, 21–25.

(Togawa *et al.*, 2015; Wang *et al.*, 2017). As magnetic field is increased, the number of solitons in a confined space becomes smaller, and the distance between the solitons becomes larger. Using Lorentz microscopy, Togawa *et al.* were able to image solitons in a 1 μm domain as the magnetic field was changed, and could see the number of solitons decrease with increasing magnetic field. Togawa, *et al.* also measured the magnetoresistance of a 10 μm sample. As the number of solitons in the sample decreased, the resistance was observed to decrease in steps. Each soliton contributes to the resistance, so that as the number of solitons decreases with increasing magnetic field, the magnetoresistance is negative. Wang, *et al.* extended these ideas by cleaving single crystals down to 28–280 nm in thickness (thinner than the magnetic domain size) and measuring the magnetoresistance. At thicknesses above the period of the helix (~ 48 nm), large steps in the magnetoresistance were observed corresponding to large relative changes in the winding number. When the samples were thinner than 48 nm, it was observed that there were no steps in the magnetoresistance in agreement with theoretical models that predict no solitons in such thin samples.

The Electrical Magnetochiral Effect

The electrical magnetochiral effect (EMC) involves the non-reciprocal transport of electrons and is described by

$$R(H, I) = R_0(1 + \gamma\mu_0 H \cdot I).$$

Here *R* is the resistance of the sample, and it changes depending on whether the current is flowing in the same direction as the magnetic field, or in the opposite direction. The term $R_0\gamma\mu_0 H \cdot I$ is known as the EMC resistance, R_{EMC} . To determine R_{EMC} , an ac current $I = I_0 \sin \omega t$ is applied to the sample and using a lock-in amplifier the 2nd harmonic is measured. The EMC voltage is given by:

$$V_{\text{EMC}}(t) = IR_{\text{EMC}} = \frac{\gamma}{2} \mu_0 R_0 I_0^2 H \left[1 - \sin \left(2\omega t + \frac{\pi}{2} \right) \right].$$

Since V_{EMC} is odd in magnetic field, R_{EMC} is determined by calculating $[R^{2\omega}(H, I) - R^{2\omega}(-H, I)]/2$.

The EMC of CrNb₃S₆ was measured by Aoki *et al.* in 2019 (Aoki *et al.*, 2019). The measurement was motivated by a previous measurement of EMC on MnSi (Yokouchi *et al.*, 2017) in which the signal was enhanced above the magnetic ordering temperature and close to the forced ferromagnetic phase, but suppressed at low fields and temperatures. As CrNb₃S₆ only has one helical axis, it is considerably simpler than MnSi and the effect of helical order on the EMC should be easier to understand.

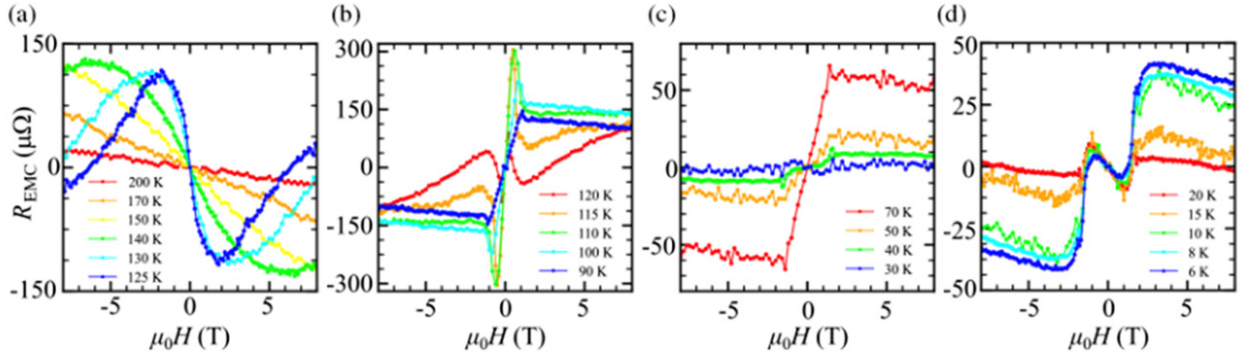


Fig. 4 Measurement of R_{EMC} in CrNb_3S_6 by Aoki, *et al.* at the indicated temperatures. Reproduced with permission from Aoki, R., Kousaka, Y., Togawa, Y., 2019. Anomalous nonreciprocal electrical transport on chiral magnetic order. *Phys. Rev. Lett.* 122, 057206.

Fig. 4 shows the measured R_{EMC} in CrNb_3S_6 . For non-magnetic chiral materials, R_{EMC} is expected to vary linearly with H , and that is what is observed in CrNb_3S_6 at 200 K, well above its 121 K ordering temperature. The sign of R_{EMC} is negative above T_C and positive below T_C . As the sample is cooled, R_{EMC} becomes much larger and becomes non-linear with field.

Fig. 5 shows a contour map of the normalized EMC coefficient, $\hat{\gamma} = \gamma S = (S/\mu_0 R_0 I) \times \partial R_{\text{EMC}}/\partial H$, where S is the cross-sectional area of the sample. What is clear in **Fig. 5** is that the EMC effect is strong in CrNb_3S_6 near phase boundaries and also in the chiral conical phase. In fact, in the conical phase, the contribution of magnetism to $\hat{\gamma}$ is three orders of magnitude greater than the non-magnetic contribution. Unfortunately, our theoretical understanding of these effects is not well-developed, and a microscopic understanding is lacking at present.

Emergent Inductance

Along with resistors, capacitors, and transformers, inductors are one of the basic passive components of electronics. As an inductor is typically made from a coil of wire, an inductor stores energy in its magnetic field, $U = \frac{1}{2}LI^2$, where U is the energy, L is the inductance, and I is the current. Because the inductance of a coil is proportional to the volume of the coil, inductors are difficult to miniaturize (Nagaosa, 2019). Also, unlike capacitors, the performance of practical inductors falls far short of the ideal, making inductors an attractive target for innovation. The relationship between the voltage and the current in an inductor is given by $V = L \frac{dI}{dt}$, and this is the key functionality that needs to be reproduced in any new technology.

In 2019 it was proposed by Nagaosa that helimagnets might serve as practical inductors that could readily be miniaturized (Nagaosa, 2019). The idea is that when itinerant electrons flow in a material containing a spin texture they acquire a Berry phase that acts as an effective electromagnetic field, called the emergent electromagnetic field. In the continuum limit, the emergent magnetic field (b_i) and electric field (e_i) are given by:

$$b_i = \frac{\hbar}{8\pi e} \epsilon_{ijk} \mathbf{n} \cdot (\partial_j \mathbf{n} \times \partial_k \mathbf{n})$$

$$e_i = \frac{\hbar}{2\pi e} \mathbf{n} \cdot (\partial_i \mathbf{n} \times \partial_t \mathbf{n})$$

Where $\mathbf{n}$ is a unit vector parallel to the local magnetization, ϵ_{ijk} is the Levi-Civita symbol, and the Einstein summation convention is assumed. Nagaosa calculated the emergent electric field associated with the spiral magnetic structure given by:

$$\mathbf{n} = \eta_1 \cos(\mathbf{Q} \cdot \mathbf{r} + \psi) + \eta_2 \sin(\mathbf{Q} \cdot \mathbf{r} + \psi) + \eta_3 \mathbf{m}.$$

Here η_1 , η_2 , and η_3 are unit vectors, $\mathbf{Q}$ is the wavevector of the spiral, and $\mathbf{m}$ represents the magnetization developed when a current flows along $\mathbf{Q}$. For a pure helimagnet, $\mathbf{m} = 0$, but when a current is applied the magnetization tilts a bit. The emergent electric field along the direction of η_3 is:

$$e_{\eta_3} = \frac{\hbar Q}{2e} \frac{\partial m}{\partial t}.$$

Nagaosa then shows that m is proportional to the current, and calculates the inductance as:

$$L \cong \frac{\pi \gamma \hbar \ell}{2e \lambda A j_{\text{int}}},$$

where ℓ and A are the length and cross sectional area of the sample, λ is the domain wall width, $\lambda = \pi/Q$, γ is a constant of order unity, and j_{int} is the threshold current density. Note that since the cross-sectional area is in the denominator, the inductance increases as the device is made smaller.

These ideas received experimental verification in 2020, when a device made from the short period helimagnet $\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ was fabricated and its inductance measured (Yokouchi *et al.*, 2020). The device was about 300 nm thick, 5 μm wide, and about 15 μm

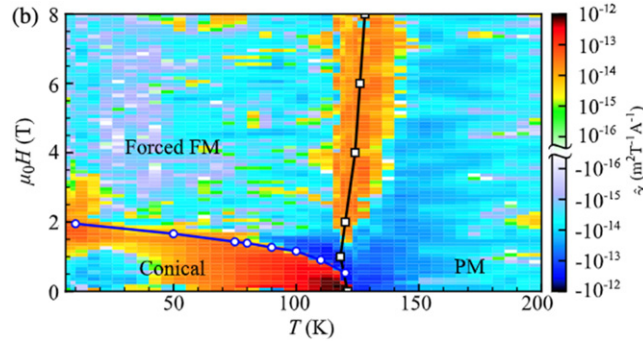


Fig. 5 Contour map of the normalized EMC coefficient, $\hat{\gamma}$, in CrNb₃S₆. Note that the intense blue areas have a large and negative coefficient. Reproduced with permission from Aoki, R., Kousaka, Y., Togawa, Y., 2019. Anomalous nonreciprocal electrical transport on chiral magnetic order. Phys. Rev. Lett. 122, 057206.

long. At 6.5 K, current density $3.3 \times 10^8 \text{ A m}^{-2}$, $f = 10 \text{ kHz}$, and no applied magnetic field, the inductance was about 10^{-7} henry. For comparison, inductors in smartphones are typically $0.6 \times 0.3 \times 0.3 \text{ mm}^3$ and have an inductance of about 3×10^{-7} henry. It is interesting that the inductance of Gd₃Ru₄Al₁₂ is negative, which is not possible for conventional inductors. Negative inductance also has potential applications, such as high speed circuits and chaotic oscillators (Yokouchi *et al.*, 2020). Emergent inductance was recently observed above room temperature in the short-period Yoshimori-type helimagnet YMn₆Sn₆ ($T_N \sim 330 \text{ K}$) (Kitaori *et al.*, 2021). Intriguingly, the value and sign of the inductance was observed to vary with temperature, magnetic field, and current density, thus pointing the way toward new electronic functionalities.

Control of Spin Helicity

In a Yoshimori-type helimagnet, in contrast to a Dzyaloshinskii-type helimagnet, both right-handed and left-handed spirals are expected to be present with equal probability and to form domains. In this case the handedness of the spiral is an emergent, internal degree of freedom that in principle can be used to encode information. Very recently, the Onose group has shown how this can be done (Jiang *et al.*, 2020). The key insight of Onose is that by applying both an electrical current and a magnetic field one can stabilize a right-handed or left-handed spiral. The way this works is as follows. If a magnetic field is applied parallel to the helical axis, the spins will tilt in the direction of the magnetic field irrespective of the handedness of the helix. However, if current is applied along the direction of the helix, the spins will tilt either in the same direction as the current or opposite to the current depending on the handedness of the spiral. When both magnetic field and current are applied, switching the direction of current will stabilize either a left-handed or right-handed spiral.

This effect was experimentally demonstrated in MnP. MnP is centrosymmetric and becomes a Yoshimori-type helimagnet below about 60K. The sample was first “poled” in analogy to a ferroelectric by first applying a large enough magnetic field to change the conical magnetic structure to a fan structure. Then an electrical current was applied and the magnetic field was reduced slowly until the sample was back in the conical phase. To determine the helicity of the poled sample, the 2nd harmonic resistivity was measured to probe the electrical magnetochiral effect. The sign of this effect is sensitive to the handedness of the spiral. Using these measurements, it was demonstrated that it was possible to stabilize both right-handed and left-handed spirals. Of course, many challenges remain before the control of the helicity degree of freedom could be used in a practical device. One challenge is instantaneous switching, which in principle could be possible by applying a current with a sufficiently high current density. Another challenge involves getting rid of high magnetic fields, which may be possible if a polarized spin current is used (Jiang *et al.*, 2020).

Conclusion: Skyrmions and Beyond

When a magnetic field is applied to a helical magnet, it often results in rich behavior and a complex phase diagram. In this article, we have mainly tried to focus on the properties and applications of the helimagnets themselves, and not some of the other spin structures that can form in applied fields. But one such spin structure is so important that we need to discuss it at least briefly.

In the case of the monoaxial chiral helimagnet, we saw that a magnetic field caused the formation of 1D magnetic solitons. Such magnetic solitons can exist in higher dimensions as well, and are called “skyrmions.” Skyrmions are nanometer-scale twisting magnetic cylinders embedded into a ferromagnetic background. The existence of skyrmions was first discussed by Bogdanov and Yablonskii in 1989 (Bogdanov and Yablonskii, 1989), but it was not until 2009 that a skyrmion lattice was observed experimentally in MnSi using small angle neutron scattering (Mühlbauer *et al.*, 2009). In 2010 single skyrmions were imaged in real space in a transmission electron microscope using a technique called Lorentz microscopy (Yu *et al.*, 2010). Skyrmions can be made to move by applying an electrical current, and are promising candidates for electronic applications such as high-density memory and logic circuits. Skyrmions have rapidly evolved into a vast field and there are many reviews. One recent and particularly detailed

review is by Tokura and Kanazawa (Tokura and Kanazawa, 2021). Another good overview is the “2020 Skyrmionics Roadmap,” with contributions from a number of leading researchers (Back *et al.*, 2020).

In summary, helimagnets are relatively simple magnetic structures but lead to many interesting and potentially useful functionalities. The pitch of the helix represents a new length scale in a solid, and is often incommensurate with the underlying crystalline lattice. The chirality of the helix is a new degree of freedom in a solid that can be used to encode information. The interaction of itinerant electrons with the helical magnetic structure leads to both emergent inductance and a large electrical magnetochiral effect. Lastly, when magnetic fields are applied to helimagnets, it can lead to new and interesting magnetic structures, including 1D solitons in monoaxial chiral helimagnets and skyrmions in other systems.

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Recent Developments in Hard Magnetic Nanostructured Materials

Nguyen Hoang Nam, Nguyen Hoang Hai, and Nguyen Hoang Luong, Nano and Energy Center, University of Science, Vietnam National University, Hanoi, Vietnam

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Abstract

Permanent magnet materials are essential components in many electric and electronic devices ranging from computer hard-disk drives to mobile phones, motors, generators, medical devices, and home appliances. The development of permanent magnets with enhanced properties is in high demand. This chapter reviews the recent developments in hard magnetic nanostructured materials. Progress made in rare-earth- and rare-earth-free hard magnetic nanostructured materials is summarized, with an in-depth analysis of their magnetic properties and applications.

Key Points

- There are two types of rare-earth and rare-earth-free hard magnetic materials.
- Correlation between the micro/nanostructures and hard magnetic properties.
- Magnetic exchange couplings in core/shell nanostructures, nanocomposites, and multiphase magnetic systems.
- Tailoring hard magnetic properties via chemical doping, synthesis optimization and heat treatment.

Introduction

Permanent magnet materials are essential components in many electric and electronic devices such as computer hard-disk drives, mobile phones, motors, generators, medical devices, and home appliances (Gutfleisch *et al.*, 2011). These materials possess high saturation magnetization (M_s), high magnetocrystalline anisotropy constant (K_u), and high coercivity (H_c), with the maximum energy product $(BH)_{\max}$. $(BH)_{\max}$ is the figure of merit used to characterize the strength of a permanent magnet. Since most of the permanent magnets are used at or above room temperature, relevant permanent magnet materials should also have high Curie temperature (T_C).

Although permanent magnets have been used for more than one thousand years, the significant breakthrough only occurred in the 1960s with the discovery of rare-earth permanent magnets (RPMs) in several intermetallic RCO_5 type compounds (Strnat *et al.*, 1967). RPMs are considered to experience three-generation developments (Poudyal and Liu, 2013; Yue and Hadjipanayis, 2017). Magnets based on SmCo_5 compound were considered the first generation of RPMs (Strnat *et al.*, 1967). These magnets exhibit large coercivity and energy products as well as good thermal stability which is desirable in applications at high temperatures. The second generation of RPMs based on the $\text{Sm}_2\text{Co}_{17}$ compound with the addition of minor amount of Cu, Fe and Zr was soon discovered (Strnat, 1972; Ojima *et al.*, 1977; Mishra *et al.*, 1981; Ray and Liu, 1992; Hadjipanayis *et al.*, 2000). In 1984, new magnets based on the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase were reported by Sagawa *et al.* (1984) and Croat *et al.* (1984a). These new Nd-Fe-B magnets exhibit much higher energy products compared to the Sm-Co-based magnets, and the new Nd-Fe-B magnets were thus called the third generation of RPMs.

As pointed out by Rivoirard and Givord, our knowledge of the magnetism of matter indicates that the hard magnetic properties of rare-earth transition metal compounds such as $\text{N}_2\text{Fe}_{14}\text{B}$ are close to the optimum properties which can be shown by high anisotropy compounds (Rivoirard and Givord, 2006). Thus, new materials with improved properties are in high demand. Nanostructuring of magnetic materials may improve properties of the materials. These systems may exhibit specific properties because their dimensions are of the order of the domain wall width, dimension defining length scale of magnetization processes (Rivoirard and Givord, 2006; Madugundo *et al.*, 2018). Nanostructured material is defined by the International Organization for Standardization (ISO), a worldwide federation of national standards bodies, as a material having internal or surface structure in the nanoscale. Nanoscale is size range from approximately 1 nm to 100 nm (ISO/TS 80004-4, 2011).

The Nd-Fe-B permanent magnets exhibit the highest energy product of 474 kJ m^{-3} (almost 60 MGOe) (Matsuura, 2006). The thermal stability of Nd-Fe-B magnets can be improved by adding the rare-earth elements Dy and Tb. The SmCo-based permanent magnets show moderate energy products of 294 kJ m^{-3} (~ 36 MGOe) and high Curie temperature (up to 800°C) (Niarchos *et al.*, 2015). These two types of RPMs are widely used today. However, the rare-earth elements including Nd, Sm, Dy, and Tb are expensive, and their supply suffers a high risk (Mohapatra and Liu (2018) and references therein). Thus, much attention is paid to research on rare-earth-free hard magnetic materials such as FePt, FePd, FeCo, Fe_{16}N_2 , FeNi, Fe_3Se_4 , Mn-based alloys. Many rare-earth- and rare-earth-free hard magnetic materials are included in Fig. 1 (Coe, 2020).

In this chapter, we provide a brief review on recent advances in the research in representative hard magnetic nanostructured materials. Section “Rare-Earth-Based Hard Magnetic Nanostructured Materials” is devoted to an overview of rare-earth hard magnetic materials. In Section “Rare-Earth-Free Hard Magnetic Nanostructured Materials” a brief review on rare-earth-free hard magnetic materials is given.

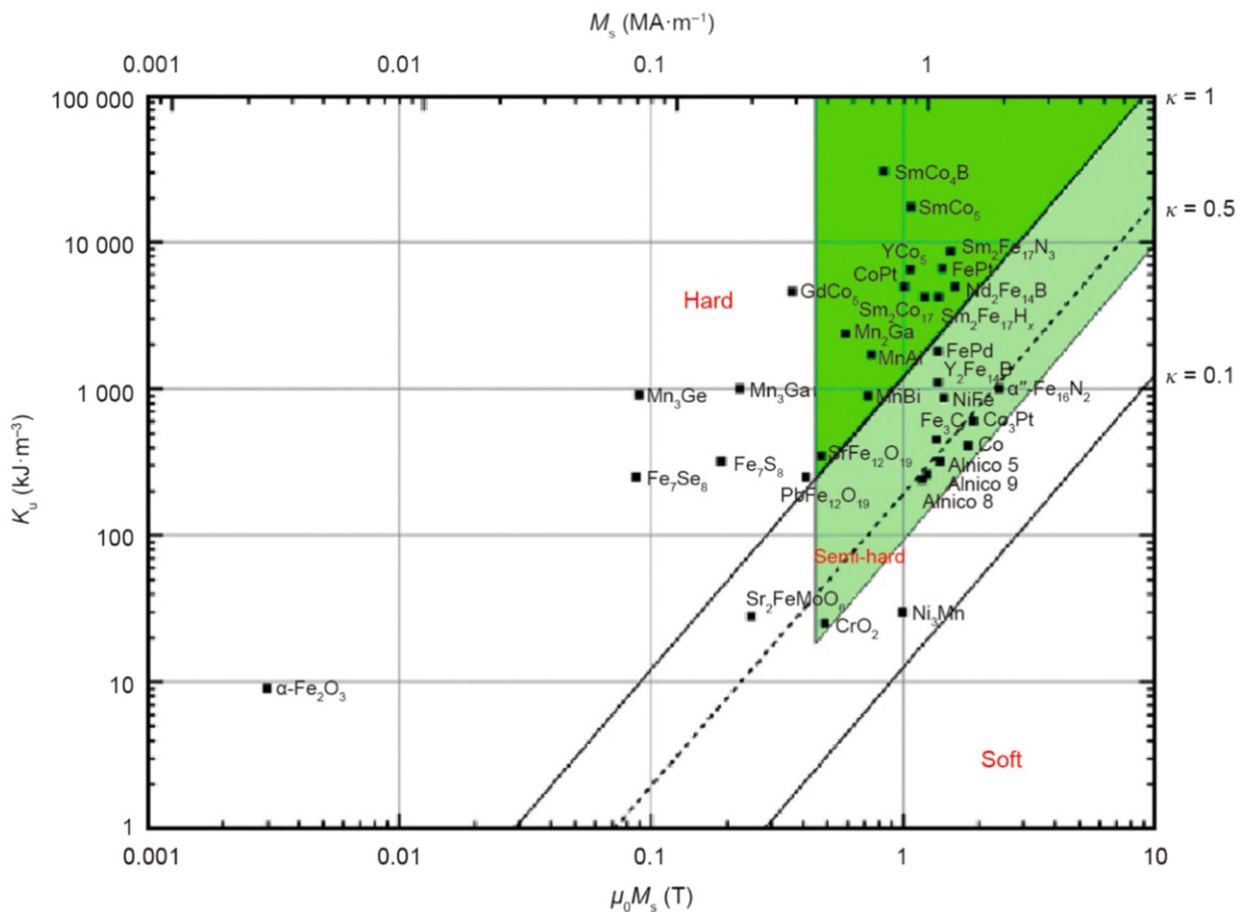


Fig. 1 Plots of anisotropy K_u as a function of polarization $\mu_0 M_s$ for a wide variety of magnetic materials with uniaxial anisotropy. Hard materials in the bright green area can be used to produce efficient magnets of any shape. Semi-hard materials in the pale green area can be used to make oriented magnets with a shape-limited energy product. Solid and dotted lines correspond to $\kappa = 1, 0.5$, and 0.1 . The magnetic hardness parameter κ is defined as $\kappa = (K_u / \mu_0 M_s^2)^{1/2}$, where K_u is the anisotropy energy and M_s is the saturation magnetization. Reproduced from Coey, J.M.D., 2020. Perspective and prospects for rare earth permanent magnets. *Engineering* 6, 119–131.

Rare-Earth-Based Hard Magnetic Nanostructured Materials

Sm-Co-Based Nanostructured Materials

SmCo₅ magnets

The SmCo_5 compound has a hexagonal structure with the easy axis along the c -axis. In the Sm-Co system, Co is responsible for high M_s , whereas high magnetocrystalline anisotropy is associated with Sm. Different approaches were elaborated to synthesize nanostructured SmCo_5 magnets exhibiting improved properties. Synthesis techniques such as ball milling, melt spinning, mechanochemical synthesis, and chemical synthesis have been used to prepare nanostructured powders or nanoparticles of SmCo_5 . By using mechanical alloying with appropriate annealing, Ding *et al.* synthesized nanostructured SmCo_5 powders having coercivity above 50 kOe (3980 kA m⁻¹) (Ding *et al.*, 1993). Using surfactants during ball milling not only influences the size and shape of the nanoparticles but also plays an important role in the formation of nanoflakes (Cui *et al.*, 2010). By using one-step surfactant-assisted ball milling (SABM), Cui *et al.* prepared magnetically anisotropic SmCo_5 nanoflakes with [001] out-of-plane texture (Cui *et al.*, 2010). The nanoflakes with thickness of 8–80 nm and length 0.5–8 μm consist of fine grains of 4–8 nm as revealed by microstructure examination and exhibit H_c of about 18 kOe (1433 kA m⁻¹). By using SABM method, Akdogan *et al.* synthesized SmCo_5 nanoparticles of an average size of 5–6 nm having coercivity of 18.6 kOe (1480 kA m⁻¹) (Akdogan *et al.*, 2009). Recently, Zuo *et al.* used a novel method of solid particle (NaCl) and surfactant co-assisted ball milling to synthesize ultrathin SmCo_5 nanoflakes (Zuo *et al.*, 2016). The obtained nanoflakes with average thickness less than 50 nm exhibit high H_c of 23 kOe (1831 kA m⁻¹). Liu *et al.* (1992) synthesized SmCo_5 nanoparticles by the mechanochemical method and obtained H_c value of larger than 65 kOe (5174 kA m⁻¹). These high coercivity values appear to be a result of the nanocrystalline structure developed by mechanical alloying and heat treatment (Liu *et al.*, 1992). Gabay and Hadjipanayis succeeded in the development of SmCo_5 nanoparticles using a mechanochemical synthesis (Gabay and Hadjipanayis, 2015). Their obtained nanoparticles showed

high H_c of 45 kOe (3582 kA m^{-1}), which are a good candidate for making anisotropic exchange-coupled nanocomposites. Shen *et al* prepared anisotropic SmCo_5 nanoplates by self-assembly of $\text{Sm}(\text{OH})_3$ nanorods and Co nanoparticles, followed by CaO coating and reductive annealing (Shen *et al.*, 2018). They showed that aligned SmCo_5 nanoplates exhibit large coercivity, reaching 30.1 kOe (2396 kA m^{-1}). Very recently, Dong *et al* synthesized dispersible SmCo_5 nanoparticles by co-precipitating a precursor containing amorphous $\text{Sm}(\text{OH})_3$ and nanoscale $\text{Co}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ crystallites (Dong *et al.*, 2019). These authors obtained the SmCo_5 nanoparticles with the coercivity of 66–72 kOe ($5253\text{--}5731 \text{ kA m}^{-1}$), the largest yet reported for permanent magnet nanoparticles.

New consolidation methods such as hot compaction, hot deformation, and spark plasma sintering (SPS) have been employed to produce bulk nanocrystalline SmCo_5 magnets. By using SPS Zhang *et al* prepared bulk nanocrystalline SmCo_5 magnet with a high coercivity (Zhang *et al.*, 2010). They obtained the magnet reaching high H_c of 28.5 kOe (2269 kA m^{-1}) and exhibiting good thermal stability with a coercivity coefficient (β) of $-0.15\%/K$. By using hot compaction, Zheng *et al* synthesized bulk nanocrystalline SmCo_5 magnets from nanoflakes (Zheng *et al.*, 2011). The hot compacted magnet had a high H_c of 14.8 kOe (1178 kA m^{-1}). In 2011 Gabay *et al* studied hot-deformed SmCo_5 nanocrystalline alloys (Gabay *et al.*, 2011). These authors reported that the SmCo_5 magnet deformed at 950°C with the 94.5% height reduction exhibits $(\text{BH})_{\text{max}}$ of 18 MGOe (143 kJ m^{-3}) and H_c of 22.8 kOe (1815 kA m^{-1}). Yue *et al.* (2011) also prepared bulk nanocrystalline SmCo_5 magnets by hot deformation technique. Their samples with 70% height reduction exhibit high value of H_c of over 50 kOe (3980 kA m^{-1}). Yuan *et al* studied the orientation textures in a hot-deformed nanocrystalline SmCo_5 permanent magnet using electron backscattered diffraction technique (Yuan *et al.*, 2014). They reported that orientation textures of both grains and grain boundary planes have a significant influence on the magnetic performance of the magnet.

Nanocomposite $\text{SmCo}_5/\alpha\text{-Fe}$ magnets

Nanocomposite magnets have attracted much attention in the 1990s due to the advantage of the high anisotropy of the hard magnetic phases and the high saturation magnetization of soft magnetic phases (Kneller and Hawig, 1991). Nanocomposite magnets have a high potential to exhibit a higher energy product than the conventional single phase hard magnets (Kneller and Hawig, 1991; Skomski and Coey, 1993; Fischer and Kronmüller, 1998). With the emergence of nanomagnetism, research on SmCo_5 permanent magnet is revitalized to improve some magnetic performances with the development of nanocomposite material consisting of SmCo_5 as the hard phase and $\alpha\text{-Fe}(\text{Co})$ as the soft phase. Chu *et al* prepared bulk $\text{SmCo}_5/\alpha\text{-Fe}$ nanocomposite magnets by ball milling a mixture of SmCo_5 and nanosize iron powders (Chu *et al.*, 2003). Their nanocomposite 20% Fe-containing magnets showed a M_s of 95 emu/g ($95 \text{ Am}^2 \text{ kg}^{-1}$) and a H_c of 7 kOe (557 kA m^{-1}) (Madugundo *et al.*, 2018). Bulk $\text{SmCo}_5 + x \text{ wt\% Fe}$ nanocomposite magnets have been prepared by Rama Rao *et al* by mechanical milling and subsequent consolidation by SPS (Rama Rao *et al.*, 2007). With increasing Fe content, the magnetization increases, however, the coercivity decreases. The 5 wt% Fe-containing sample has a coercivity of 8.9 kOe (708 kA m^{-1}) and magnetization (at a maximum applied field of 7 T) of 86 emu/g ($86 \text{ Am}^2 \text{ kg}^{-1}$), while these values for 10 wt% Fe-containing sample are 7 kOe (557 kA m^{-1}) and 96 emu/g ($96 \text{ Am}^2 \text{ kg}^{-1}$), respectively. The $\text{SmCo}_5/10 \text{ wt\% Fe}$ sample was reported to have a $(\text{BH})_{\text{max}}$ of 8–10 MGOe ($64\text{--}80 \text{ kJ m}^{-3}$). The authors pointed out that the relatively lower energy products obtained in the samples are due to the randomness of the nanograins. Rama Rao *et al* investigated a nanocomposite consisting of Sm-Co-Fe intermetallic phases and Fe (Co) prepared by SPS (Rama Rao *et al.*, 2008). Their TEM studies revealed that the synthesized magnet has $\text{Sm}(\text{Co,Fe})_5$ as a major phase, with $\text{Sm}_2(\text{Co,Fe})_{17}$, $\text{Sm}(\text{Co,Fe})_2$, and $\text{Fe}(\text{Co})$ as secondary phases. The size of the nanocrystalline grains of all these phases was found to be in the range 50–100 nm. Fig. 2 shows hysteresis curves of the spark-plasma sintered SmCo_5 and samples containing 5 and 10 wt% Fe measured at 300K. As indicated in this figure, $(\text{BH})_{\text{max}}$ of the obtained SPS magnets is found to be 7.1 MGOe (56.5 kJ m^{-3}). According to Rama Rao *et al.* (2008) the low energy product in the SPS magnets can be attributed to a random assembly of the nanocrystallites of the $\text{Sm}(\text{Co,Fe})_5$ phase and the presence of the other Sm-Co-Fe secondary phases.

Various other techniques have been used to prepare Sm-Co/ $\alpha\text{-Fe}$ nanocomposite magnets. By using warm compaction Rong *et al.* (2010) synthesized $\text{SmCo}_5/25 \text{ wt\% FeCo}$ nanocomposite magnet exhibiting high $(\text{BH})_{\text{max}}$ of 19.2 MGOe (152.8 kJ m^{-3}). Hu *et al.* (2012) applied SABM, chemical coating, and hot compaction techniques to prepare bulk anisotropic $\text{SmCo}_5/\alpha\text{-Fe}$ nanocomposite magnets. This bottom-up approach of preparation allowed the authors to obtain magnets displaying a noticeable magnetic anisotropy. Their $\text{SmCo}_5/5 \text{ wt\% Fe}$ magnet possesses $M_{2.3T}$ of 78.68 emu/g and H_c of 8.02 kOe (637 kA m^{-1}). Recently, by performing temperature-gradient deformation at high stress ($\sim 1 \text{ GPa}$) and large strain ($\sim 80\%$) Li *et al.* (2017) obtained an anisotropic bulk Sm-Co/ $\alpha\text{-Fe}$ nanocomposite magnet with large $(\text{BH})_{\text{max}}$ of 26 MGOe (208 kJ m^{-3}). Current efforts to develop high-performance nanocomposite magnets are ongoing.

$\text{R}_2\text{Fe}_{14}\text{B}$ -Based Nanostructured Magnets

$\text{R}_2\text{Fe}_{14}\text{B}$ -based single-phase magnets

The nanocrystalline Nd-Fe-B ribbons exhibit higher coercivity and better chemical stability compared with sintered Nd-FeB magnets of similar composition (Yue and Hadjipanayis, 2017). Yue and Hadjipanayis also pointed out that, to date, melt-spun nanocrystalline Nd-Fe-B ribbons have become the most successful raw materials for bonded magnets (Yue and Hadjipanayis, 2017). As an effective way to synthesize nanostructured materials, the melt-spun technique was used to prepare magnetically isotropic $\text{R}_2\text{Fe}_{14}\text{B}$ ribbons (Liu *et al.*, 2011a); Croat *et al.* (1984b) prepared melt-spun Nd-Fe-B ribbons exhibiting intrinsic

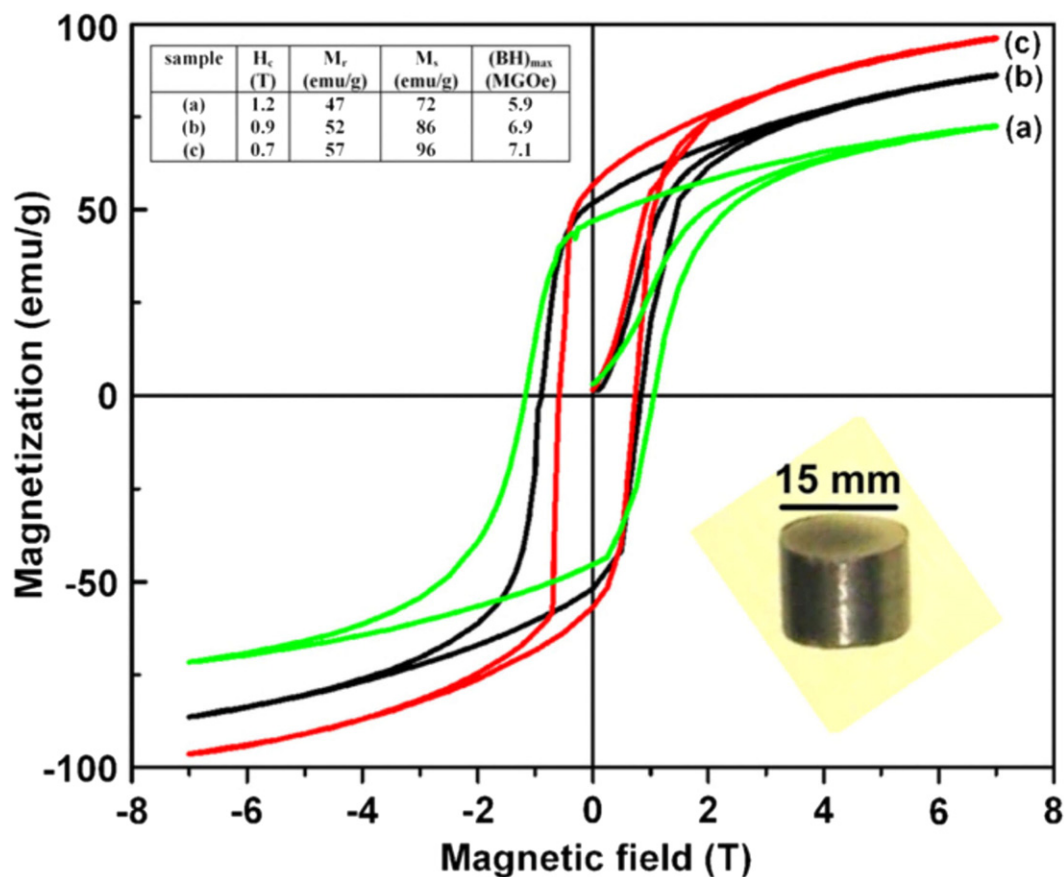


Fig. 2 Hysteresis curves of the spark-plasma sintered (a) SmCo_5 (b) 5 wt% and (c) 10 wt% Fe-containing SmCo_5 samples measured at 300K. The inset shows a typical spark-plasma sintered nanocomposite magnet. Reproduced from Rama Rao, N.V., Saravanan, P., Gopalan, R., *et al.*, 2008. Microstructure, magnetic and Mössbauer studies on spark-plasma sintered Sm–Co–Fe/Fe(Co) nanocomposite magnets. *J. Phys. D: Appl. Phys.* 41, 065001.

coercivity of up to 20 kOe (1592 kA m^{-1}). Pinkerton (1986) developed Dy–Fe–B and Tb–Fe–B based ribbons having coercivity up to 64 kOe (5094 kA m^{-1}). Liu *et al.* (2011a) studied $\text{Tb}_{14}\text{Fe}_{86-x}\text{B}_x$ ($x = 5.2\text{--}6.8$) ribbons prepared by melt-spun and obtained ultrahigh coercivity up to 77.4 kOe (6161 kA m^{-1}) for $\text{Tb}_{14}\text{Fe}_{79.6}\text{B}_{6.4}$ ribbons. This very high coercivity is attributed to the optimal ribbons' microstructure which comprises fine and uniform crystal grains.

A variety of commercialized NdFeB-based melt-spun ribbons have been synthesized into bulk nanostructured magnets by using SPS (Yue *et al.*, 2006; Liu *et al.*, 2010). Yue *et al.* (2006) obtained Nd–Fe–B magnets with remanence (B_r) of 1.34 T, coercivity of 512 kA m^{-1} , and maximum energy product ($(BH)_{max}$) of 280 kJ m^{-3} . Under optimal conditions, Liu *et al.* developed anisotropic Nd–Fe–B magnet exhibiting B_r of 1.492 T, coercivity of 1004 kA m^{-1} , and $(BH)_{max}$ of 400 kJ m^{-3} (Liu *et al.*, 2010). More recently, by tuning the current pulse ratio of power-on time to power-off time during sintering from 12: 2–2: 2, Wang *et al.* successfully reduced the thickness of the surface diffusion layer of Nd–Fe–B particles in hot pressed magnets leading to the increase of the $(BH)_{max}$ of the magnets by 27% (Wang *et al.*, 2015).

By using SABM, Cui *et al.* synthesized magnetically anisotropic $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoflakes (Cui *et al.*, 2012). These authors reported that both the addition of some low-melting-point eutectic alloy, such as $\text{Nd}_{70}\text{Cu}_{30}$, and an appropriate post-annealing can increase the coercivity of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ flakes. With an addition of 16.7 wt% $\text{Nd}_{70}\text{Cu}_{30}$ by milling for 5 h in heptane with 20 wt% oleylamine, the coercivity of $\text{Nd}_2\text{Fe}_{14}\text{B}$ flakes increased from 3.7 to 6.8 kOe ($294.5\text{--}541 \text{ kA m}^{-1}$) after annealing at 450°C for 0.5 h (Cui *et al.*, 2012). Higher H_c of 16.8 kOe (1337 kA m^{-1}) in Dy–Fe–B nanoflakes (Yue *et al.*, 2012) was achieved. This once again demonstrates that for nanostructured RPMs the higher magnetic anisotropy, the higher coercivity (Yue and Hadjipanayis, 2017).

Lee (1985) was the first to report the anisotropic nanocrystalline Nd–Fe–B permanent magnets prepared by hot deformation. This author obtained the material having an energy product of 40 MGOe (318.4 kJ m^{-3}). By using of hot deformation under optimal processing conditions, Liu *et al.* (2010) prepared the anisotropic Nd–Fe–B magnet exhibiting excellent magnetic properties with coercivity of 1004 kA m^{-1} and the maximum energy product of 400 kJ m^{-3} (Fig. 3). Rong *et al.* (2012) studied the effect of pressure loading rate on the anisotropic NdFeB nanocrystalline magnets prepared by hot deformation. These authors found that the maximum energy product of the magnets increases from 31 to 44 MGOe ($246.7\text{--}350.2 \text{ kJ m}^{-3}$) by reducing the pressure loading rate from 300 MPa/min to 50 MPa/min. Yang *et al.* (2020) reported the magnetic properties and crystallization

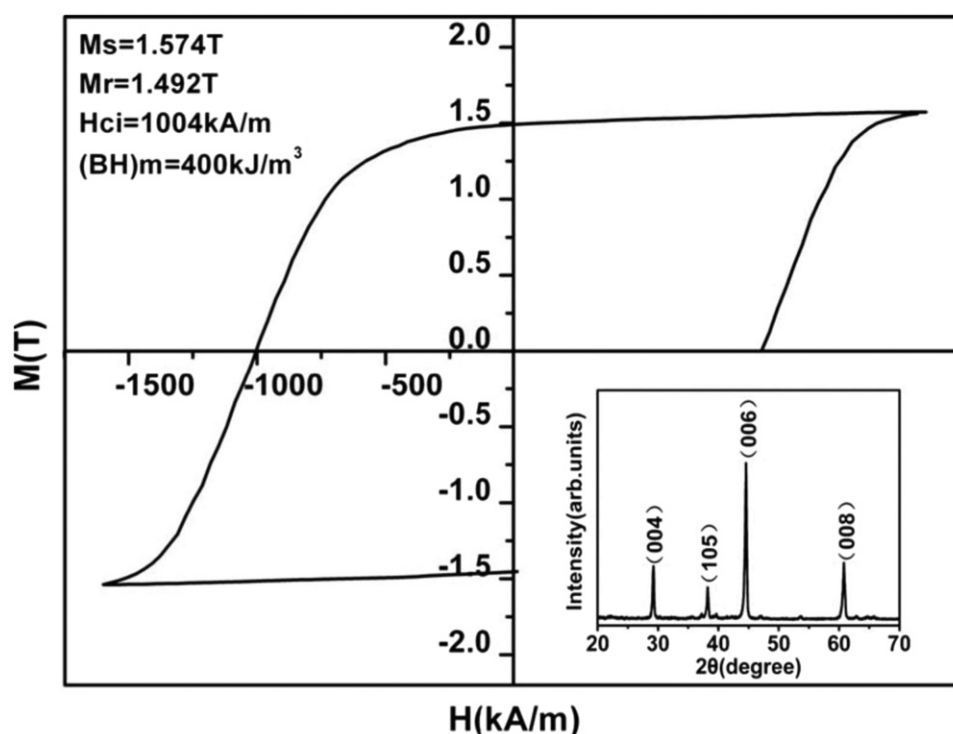


Fig. 3 Hysteresis loop of hot deformed Nd-Fe-B magnet prepared under optimal conditions. The inset shows the corresponding XRD pattern. Reproduced from Liu, W.Q., Cui, Z.Z., Yi, X.F., *et al.*, 2010. Structure and magnetic properties of magnetically isotropic and anisotropic Nd-Fe-B permanent magnets prepared by spark plasma sintering technology. *J. Appl. Phys.* 107, 09A719.

behavior of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ single-phase magnets prepared by rapid thermal processing using electron-beam heating. The crystallization temperature of the rapid thermal processed ribbons decreased by about 248°C compared to that of the ribbons prepared by the conventional annealing method.

R₂Fe₁₄B-based nanocomposite magnets

The nanocomposite magnets were expected to exhibit higher remanence, higher coercivity, and higher energy product compared with their single-phase counterparts. The high performances of nanocomposite magnet materials are due to the exchange interactions between the hard and soft phases. In addition, the fabrication cost of rare-earth nanocomposite magnets is substantially reduced because these materials contain less rare-earth elements. In 1989, Coehoorn *et al.* were the first to prepare isotropic $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B}$ nanocomposite magnets by melt-spinning (Coehoorn *et al.*, 1989). Their samples exhibited the energy product of 95 kJ m^{-3} . Later, Withanawasam *et al.* synthesized $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposite magnets with the composition of $\text{Nd}_{3.85}\text{Tb}_2(\text{Fe-Nb-B})_{94.15}$, exhibiting coercivity of 4.5 kOe (358 kA m^{-1}) (Withanawasam *et al.*, 1994).

Fast consolidation techniques are needed to obtain bulk nanocomposite magnets exhibiting desirable microstructure and magnetic properties. Yue *et al.* used SPS to prepare the bulk nanocomposite $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ magnets (Yue *et al.*, 2006). Under the optimal sintering conditions, these authors obtained the magnet with the composition of $\text{Nd}_8\text{Fe}_{86}\text{B}_6$ possessing B_r of 0.99 T , coercivity of 386 kA m^{-1} (4.8 kOe) and $(\text{BH})_{\text{max}}$ of 101 kJ m^{-3} (12.6 MGOe).

In recent years, the development of bulk anisotropic nanocomposite magnets has also drawn attention. Yue *et al.* (2008) studied the effect of $\alpha\text{-Fe}$ content on the structure and magnetic properties of bulk anisotropic $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposite magnets synthesized by hot deformation. The magnet with 2 vol% $\alpha\text{-Fe}$ exhibits a maximum energy product 395 kJ m^{-3} (49.38 MGOe). The increase of the $\alpha\text{-Fe}$ content from 2 to 5 vol% leads to the deterioration of $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystalline texture, leading to the degradation of magnetic properties of the magnets (Yue *et al.*, 2008). Liu *et al.* (2009) investigated the $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanocrystals *c*-axis crystal texture development in Nd-lean amorphous $\text{Nd}_9\text{Fe}_{85}\text{B}_6$ alloy during hot deformation at a large uniaxial stress ($\sim 310 \text{ MPa}$). The authors demonstrated that during the hot deformation processes, a (00 l) texture for $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanocrystals develops in the Nd-lean amorphous $\text{Nd}_9\text{Fe}_{85}\text{B}_6$. This texture formation is attributed to a preferential nucleation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanocrystals with a (00 l) orientation in the amorphous matrix during the hot deformation processes under large stress. Yang *et al.* (2020) reported the magnetic properties and crystallization behavior of the $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposite magnets synthesized by rapid thermal processing using electron-beam heating. A strong synergistic crystallization effect of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\alpha\text{-Fe}$ phases in the $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ magnets was observed under the rapid thermal processing. According to these authors, better magnetic properties in $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposite were achieved using rapid thermal processing in comparison with the conventional annealing method.

Rare-Earth-Free Hard Magnetic Nanostructured Materials

Alnico and Hard Magnetic Ferrites

Alnico magnets

The Alnico magnets containing Al, Ni and Co are not as strong as R magnets but exhibit good thermal stability and mechanical properties. They occupy a certain market share along with ferrite and R magnets. Alnico can be considered as the first modern permanent magnet, and improvements in its magnetic properties were promoted during the 1950–60s by optimizing alloy structure and synthesis (Campbell and Julien, 1961; Julien and Jones, 1965). By increasing Co content, the magnetization becomes lower, but the coercivity H_c is improved (Alnico-2). In Alnico-5, the $(BH)_{\max}$ was improved by nearly 5 times by adding Co content to nearly double and Alnico-8 was designed for a high H_c of 1.7 kOe (135 kA m^{-1}). In that period of time, the further increase of Co content, the addition of Ti, and the novel thermal magnetic treatment all affected these improvements of Alnico magnetic properties. However, the interest in further improvements of Alnico magnets has almost disappeared after the prominence of the much stronger SmCo_5 magnet. In 2014, the prediction of Zhou *et al* reignited interest in Alnico by showing that the $(BH)_{\max}$ of Alnico could theoretically reach 20 MGOe (159.2 kJ m^{-3}) based on the use of TEM/atom probe tomography and a model of micromagnetism (Zhou *et al.*, 2014).

The Alnicos are the materials with a microstructure containing ferromagnetic particles, such as FeCo-rich phases, embedded in a weakly magnetic matrix, such as NiAl rich phases (Lewis and Jimenez-Villacorta, 2013). Their magnetic characteristics, M_s and T_C , mainly derive from the cubic structured FeCo components, and their magnetocrystalline anisotropy (K_u) is lower than that of the Nd-Fe-B magnet. Zhou *et al* showed Alnico magnets containing randomly dispersed FeCo parallelepipeds with low H_c (Zhou *et al.*, 2014, 2017, 2018). A microstructure consisting of elongated FeCo was achieved by applying the magnetic annealing process (Luborsky *et al.*, 1957). In principle, the shape anisotropy of the FeCo parallelepipeds acts as a basis of coercivity. However, the coercivity is not only originated from magnetocrystalline anisotropy, but also from non-perfect microstructures which allow magnetization reversal to lower energy state (Zhou *et al.*, 2014). The modern characterization tools and the computational modeling allow a deep look into the nanostructure and the transition of the alloys into a magnetic Fe–Co-rich phase and an Al–Ni-rich phase. Studies of some commercial Alnico alloys show that the doping of alloying elements such as Cu and Ti can influence the microstructure of the Alnico (Sun *et al.*, 2015; Zhou *et al.*, 2014, 2017, 2018). It is also sensitive to the crystallographic orientation of the initial phase along the applied magnetic field direction. In addition, atom probe measurements provide detailed phase evolution characterization, including metastable transitional phases, together with the Alnico decomposition. Recently, the composition and the applied magnetic field on the formation of the transitional phases have been precisely measured, which improved the phase properties and have offered new methods for enhanced coercivity.

Hard magnetic ferrites

Ferrites are the cheapest and the most popular permanent magnets. These magnets have the compositions of $\text{MO} \cdot 6\text{Fe}_2\text{O}_3$ (where M is Ba, Sr, or Pb) and are composed of fine particles with hexagonal crystal structure (Haneda and Kojima, 1973; Jing *et al.*, 2015; Garcia *et al.*, 2001; Stingaciu *et al.*, 2015; Tenaud *et al.*, 2004). Among them, the Ba-based compounds (barium ferrite or hexaferrite), which are usually called ceramic magnets, are the most used permanent magnets, while Pb-based compositions are not popular due to toxicological reasons. These ferrites have reasonable coercivities but a relatively low magnetization due to the existence of both ferromagnetic and antiferromagnetic couplings between Fe magnetic moments (Mohapatra and Liu, 2018). They have the saturation magnetization M_s of $\sim 33\%$ of that of the Alnico and $\sim 25\%$ of that of Nd-Fe-B magnets, with the $(BH)_{\max}$ of ~ 4 MGOe (31.8 kJ m^{-3}) at room temperature. Selectively reducing the net magnetization of one sublattice can increase the ferrite magnetization by increasing the difference in the moment between the two sublattices. However, this action decreases the Curie temperature T_C (near 450°C) by reducing the interatomic exchange couplings. The overall magnetization shows a high sensitivity to temperature of around $-0.2\% \text{ K}^{-1}$, which is an order of magnitude bigger than that of the Alnico. Alternatively, the coercivity of the ferrites varies by the exchange coupling in the sublattice, which have an easy magnetization direction parallel with the hexagonal c -axis. The significant enhancements of H_c can be achieved by doping of the La atoms to Sr sites and Co atoms to selective sites of Fe, but phase stability limits the extent of doping (Yang *et al.*, 2015). In parallel, a high H_c value can be observed by controlling of the size and morphology of the ferrites within a single domain. Due to the increase of the average crystallite size within a single domain, cobalt ferrite nanocrystals prepared under size-tuning conditions have a H_c value of 9.4 kOe (748.2 kA m^{-1}) (Cedeño-Mattei *et al.*, 2010). The H_c values of the cobalt ferrite nanocrystals with a size in the range of 11–19 nm varied between 114 Oe and 4.4 kOe (9.1 kA m^{-1} and 350.1 kA m^{-1}), respectively, by changing the starting Fe:Co mole ratio (Cedeño-Mattei *et al.*, 2012). This variation in H_c values largely came from the tuning of the crystal size, the surface anisotropy, the distribution of cations between tetrahedral and octahedral sites, as well as the exchange coupling interaction between soft and hard magnetic phases. In nanocomposite of $\text{CoFe}_2\text{O}_4/\text{SrFe}_{12}\text{O}_{19}$, which has been synthesized by the electrospinning and calcination processes, increases of the saturation magnetization to 62.8 emu/g ($62.8 \text{ Am}^2 \text{ kg}^{-1}$) and of the coercivity to 2.29 kOe (182.2 kA m^{-1}) were observed by the tuning of the average crystallite size of the soft and hard phases (Pan *et al.*, 2015), while the exchange coupling between spin-canting layers at the interface of a soft magnetic MnFe_2O_4 shell and a hard magnetic CoFe_2O_4 core also caused an increase in H_c (Moon *et al.*, 2017). The ferrites are the most widely used permanent magnets when they account for nearly 90% by weight of the global production of magnetic materials. They are made of inexpensive, easy-to-handle elements. Furthermore, in the form of oxides, the ferrites own excellent anti-corrosion stability, making them applicable in electrical machines.

Mn-Based Hard Magnets

MnBi hard magnets

Mn alloyed with other elements such as Bi, Al, Ga and Si, etc., can form hard magnets and have attracted much interest due to their high T_C values and magnetocrystalline anisotropy (Mohapatra and Liu, 2018; Cui *et al.*, 2018; Chen and Aagard, 1970; Das *et al.*, 2016; Pasko *et al.*, 2014; Poudyal *et al.*, 2016; Zhu *et al.*, 2012). Among these materials, the bulk MnBi alloys with NiAs-type hexagonal structure have a high uniaxial anisotropy of $K_1 \sim 16 \text{ Merg cm}^{-3}$ (1.6 MJ m^{-3}) with a high T_C of 633K. Interestingly, the bulk MnBi magnet has the coercivity H_c linearly increasing from the value of 6.5 kOe (517.3 kA m^{-1}) at 300K to the value of 28.3 kOe (2252 kA m^{-1}) at 530K (Saha *et al.*, 2002), which may be due to the hybrid domain wall pinning (Guo *et al.*, 1993).

In general, the most interesting hard magnetic properties can be found in the low-temperature phases (LTP) of MnBi alloys. The experimental result for directionally solidified LTP MnBi is in good agreement with first principles calculations, which show that the LTP MnBi can achieve $(BH)_{\max}$ at 300K of 17.7 MGOe (140.8 kJ m^{-3}) (Park *et al.*, 2014). To prepare MnBi with high LTP ratio, some techniques have been developed, including mechanical alloying, rapid solidification, and arc melting. For instance, high-temperature annealing with separation by magnetic field was applied to synthesize a high purity MnBi alloy with the coercivity H_c at room temperature of 14 kOe (1114 kA m^{-1}), which contained over 90 wt% LTP (Yang *et al.*, 2001). Highly anisotropic MnBi powders synthesized by low energy ball milling and arc melting exhibit very high H_c of 11.7 kOe (931 kA m^{-1}), remanence ratio M_r/M_s of 0.97, and $(BH)_{\max}$ of 9 MGOe (71.6 kJ m^{-3}) (Rama Rao *et al.*, 2013). In the measured temperature range from 300K to 530K, the positive dependence on temperature of coercivity of about $1.45\% \text{ K}^{-1}$ indicates that these magnets can work at high temperatures.

A study of the magnetic moment under the influence of electron density pictures and the c/a lattice constant ratio indicates a possibility of getting higher M_s and then $(BH)_{\max}$ values by adding of elements into certain sites of LTP MnBi. A reduced MnBi particle size to around 40 nm in the multilayer-type MnBi/Al thin films caused a change from the dominant magnetization reversal process based on the movement of domain walls to the coherent rotation one (Rüdiger *et al.*, 2000). The electronic structure and magnetic properties of MnBi doped with Al and Nd were investigated using the local density functional approximation (Zhiqiang *et al.*, 1991). Significant changes in the magnetic behavior of MnBi ribbon nanostructures with decreasing in M_s and K_u but increasing in H_c , were observed by the doping of C, Fe, B, Sm, Tb, and Hf (Kharel *et al.*, 2013). Those changes were assigned to the results of the structural disorder and the competing ferromagnetic and antiferromagnetic interactions. The doping of Hf, Tb, and Sm led to a significant increase in H_c of MnBi ribbons, where a high value of 13 kOe (1034.5 kA m^{-1}) of H_c was obtained for the Hf-doped sample. The anisotropy energy of the boron doped sample increased by about 15%, while Hf and C co-doping showed the opposite effect with a small increase in both M_s and K_u . Fang *et al.* (1999) showed that large K_u and high M_r can be achieved by doping of rare-earth elements, such as Sm, Dy, or Tb, in MnBi films. For Si and Nb doped MnBi alloy, the T_C was increased from 360°C to 400°C (Kempter and Bayer, 1976). Very recently, Gabay *et al.* (2020) developed bulk magnets with energy product of up to 12 MGOe in field annealed Mn-Bi-Mg-In-Sb alloys. A small addition of In to the Mn-Bi-Mg-Sb alloys considerably improved the texture and the $(BH)_{\max}$ of the magnetic-field-annealed magnets prepared from compacted melt-spun ribbons. $(BH)_{\max} = 11.6 \text{ MGOe}$ (92.3 kJ m^{-3}) and $H_c = 8.5 \text{ kOe}$ (676.6 kA m^{-1}) were obtained for the $\text{Mn}_{50}\text{Bi}_{45}\text{Mg}_3\text{In}_{0.5}\text{Sb}_{1.5}$ magnet, whereas in the $\text{Mn}_{50}\text{Bi}_{46}\text{Mg}_3\text{In}_{0.5}\text{Sb}_{0.5}$ magnet the highest $(BH)_{\max}$ of 12 MGOe (95.5 kJ m^{-3}) was attained (Gabay *et al.*, 2020).

MnAl hard magnets

Among Mn-based magnets, low density MnAl alloy exhibits large magnetocrystalline anisotropy and good anti-corrosion properties (Cui *et al.*, 2018). The strongly ferromagnetic tetragonal τ -phase ($L1_0$) MnAl in the Mn composition range of 50–60 at% was first reported by Koch *et al.* (1960). Theoretical analysis of MnAl systems indicated rather good saturation magnetic polarization J_s values of 7.5 kG (0.75 T), magnetocrystalline anisotropy K_u value of 17 Merg cm^{-3} (1.7 MJ m^{-3}), as well as maximum magnetic energy product $(BH)_{\max}$ of 12.4 MGOe (98.7 kJ m^{-3}) with T_C of 650K (Fang *et al.*, 2016). A large anisotropy of these alloys can be achieved by the small excess of Mn, which results in the occupation of some Mn on the Al sites. The substitution results in local antiferromagnetic interaction of some Mn moments and stabilizes the high-anisotropy tetragonal phase at the same time.

In general, the τ -phase MnAl is thermodynamically unstable and can be decomposed into the stable phases of β -Mn and γ_2 -phases. To avoid this, a carbon doping can elongate the c -axis, then stabilize the tetragonal structure (Fazakas *et al.*, 2007; Zeng *et al.*, 2007). The doping of carbon enhances the M_s but reduces the T_C and likely the K_u . The $L1_0$ MnAl ordered phase can be observed by a massive phase transition from the hexagonal ϵ -phase at high temperatures, which can be achieved by rapid cooling (Fang *et al.*, 2016). An explanation for this transformation is a reaction changing the structure of the ϵ -phase to an orthorhombic structure, and continuing by a ferromagnetic τ -phase transition, not excluding nucleation and diffusion processes (Yanar *et al.*, 2002). The $L1_0$ phase can be derived via heat treatment from the ϵ -phase, which was synthesized by mechanical alloying and melt spinning. The melt-spun MnAl shows a huge unidirectional shift in the magnetic hysteresis loop observed at low temperature (Jiménez-Villacorta *et al.*, 2012), which can be explained by a phase separation with ϵ -structure, resulting in these magnetic nanocomposites' useful properties. A coercivity of 10.7 kOe (851.7 kA m^{-1}), saturation magnetization of 361.4 emu/cm^3 (0.454 T) and $(BH)_{\max}$ of 4.44 MGOe (35.34 kJ m^{-3}) were obtained at room temperature for τ -MnAl epitaxial films by Nie *et al.* (2013).

Typical coercivity and energy product values observed in the literature for MnAl alloys synthesized by melt spinning or coincide heat treatment, are around 1.5–2 kOe (119.3 – 159.1 kA m^{-1}) and 4–7 MGOe (31.8 – 55.7 kJ m^{-3}), respectively. To enhance the coercivity, another nonequilibrium synthesis process, such as the mechanical alloying, was used to reduce the MnAl particle-size. By effectively reducing the grain size, the mechanical alloying single-phase $L1_0$ -type MnAl shows a coercivity increase from the

small value of 1.7 Oe (135.3 kA m^{-1}) to 4.8 kOe (381.9 kA m^{-1}), which is almost the highest value achieved for MnAl. MnAl alloys are low-cost, however, their permanent magnetic properties are still required to improve for sharing the market with hard ferrite magnets (Feng *et al.*, 2020).

MnGa hard magnets

The ferrimagnetic MnGa materials with a tetragonal structure have attracted much interest as a material candidate for permanent magnets, spintronic applications, and magnetic recording applications due to their large perpendicular anisotropy (Kurt *et al.*, 2011; Meng *et al.*, 2016). The oriented MnGa films have a large anisotropy of $K_u = 10 \text{ Merg cm}^{-3}$ (1.0 MJ m^{-3}) (Mizukami *et al.*, 2011) and changing the composition of the films could change their magnetic properties (Zhu *et al.*, 2013). The saturation magnetization rises from 130 to 450 emu/cm³, the anisotropy increases from 8.6 to 21 Merg cm⁻³ ($0.86\text{--}2.1 \text{ MJ m}^{-3}$), and magnetic coercivity increases from 4.38 to 20.1 kOe ($384.5\text{--}1559.5 \text{ kA m}^{-1}$), when the Mn content changes from 0.76 to 1.75. Here, the large magnetocrystalline anisotropy and appropriate crystalline size could be the origin of the enhanced coercivity. A high coercivity of up to 42.8 kOe (3407 kA m^{-1}), the ultra high perpendicular magnetic anisotropy of $21.7 \text{ Merg cm}^{-3}$ (2.17 MJ m^{-3}) and the big $(\text{BH})_{\text{max}}$ of 2.6 MGOe (20.7 kJ m^{-3}) were obtained in $\text{L}_{10}\text{-Mn}_{1.5}\text{Ga}$ epitaxial films synthesized by molecular-beam epitaxy (Zhu *et al.*, 2012). These open the large possibility for these films to be applied in permanent magnets, ultrahigh density recording, and spintronics. To reduce the production cost, MnGa ferromagnetic nanoparticles have also been prepared by the solution routes (Patel *et al.*, 2018). However, low coercivity was obtained due to the reduction of a L_{10} phase content and the much smaller size of the particles compared to that of a single domain.

Mn₅Si₃ magnets

The magnetic moment of Mn atoms is bigger than those of Fe and Co. Among Mn-based compounds, Mn_5Si_3 has attracted considerable interest due to its hexagonal structure in space group $\text{P6}_3/\text{mcm}$ with potentially high magnetocrystalline anisotropy (Das *et al.*, 2016). In general, materials with high M_s and K_1 play an important role for designing new rare-earth-free permanent magnets. However, the bulk Mn_5Si_3 magnets show a paramagnetic behavior at room temperature with antiferromagnetic ordering at temperature below 100K, where their structure transforms into an orthorhombic phase (Gottschilch *et al.*, 2012; Sürgers *et al.*, 2014; Das *et al.*, 2016). Das *et al.* (2016) indicated that nanostructuring of Mn_5Si_3 compounds can advance ferromagnetic ordering under high Curie temperature T_C of $\sim 590\text{K}$. The Mn_5Si_3 nanoparticles with an average size of 8.6 nm were fabricated using a gas aggregation-type cluster-deposition method. Bulk Mn_5Si_3 is paramagnetic at room temperature and shows antiferromagnetic transitions at 99K and 66K, originating from a the hexagonal - orthorhombic structure transition at 100K (Das *et al.*, 2016). In comparison, an enhanced magnetization by about three orders of magnitude indicates a possible ferromagnetic ordering of the nanoparticles with a Curie temperature T_C higher than 300K. A T_C close to 590K for the nanoparticles was suggested from the measured $M\text{--}T$ curve at elevated temperatures. The Mn_5Si_3 nanostructures also show large saturation polarization J_s of 10.1 kG and 12.4 kG (1.01 T and 1.24 T), with an appreciable magnetocrystalline anisotropy constants K_u of 6.2 Merg cm^{-3} (0.62 MJ m^{-3}) and $12.8 \text{ Merg cm}^{-3}$ (1.28 MJ m^{-3}) at 300K and at 3K, respectively (Das *et al.*, 2016). The Mn_5Si_3 nanoparticles are successfully aligned with an external field of $\sim 5 \text{ kOe}$ (397.8 kA m^{-1}), revealing their strong magnetocrystalline anisotropy. The magnetic hysteresis loops of the aligned nanoparticles show an appreciable coercivity H_c of 1.7 kOe (153.3 kA m^{-1}) at 3K, compared to a value of 0.9 kOe (71.6 kA m^{-1}) for H_c of the isotropic nanoparticles at 300K. In Mn_5Si_3 nanorods synthesized by the solid-state reactions, the obtained saturation magnetization at 30 kOe and the coercivity were 4.63 emu/g ($4.63 \text{ Am}^2 \text{ kg}^{-1}$) and 61.5 Oe (4.9 kA m^{-1}), respectively, which are lower than values of Mn_5Si_3 nanostructures above (Lu *et al.*, 2018). These results indicate that the magnetic properties of Mn_5Si_3 nanoparticles can be tailored by many factors, such as size, structure, morphologies, etc.

Co-Based Hard Magnets

Co-Zr alloys

Due to its large magnetocrystalline anisotropy of 1.1 MJ m^{-3} with a high T_C of 773K, the Co-based $\text{Zr}_2\text{Co}_{11}$ alloy has attracted much attention as a R-free permanent magnet, which theoretically can produce a $(\text{BH})_{\text{max}}$ of 23.5 MGOe (187 kJ m^{-3}) (Ishikawa and Ohmori, 1990). Depending on the preparation method, $\text{Zr}_2\text{Co}_{11}$ crystallizes in an orthorhombic or a rhombohedral structure, where the latter phase can be tailored to achieve hard magnetic properties (Zhao *et al.*, 2014; Demczyk and Cheng, 1991). The phase diagram indicates that $\text{Zr}_2\text{Co}_{11}$ -phase generates at about 15.4 at% of Zr with a transition reaction at 1543K. To synthesize the $\text{Zr}_2\text{Co}_{11}$ samples, melt spinning processes with and without rapid solidification have been widely employed, wherein a rapid quenching after the alloy formation and a precise control of the composition are needed to observe a high phase purity. The latter method is also the process of forming nanostructure in the sample and high H_c values were obtained in rapidly solidified ribbons compared with their counterpart bulk alloys. The Zr content, alloying additives, processing conditions, and heat-treatment temperatures influence the phase constituents, microstructure, and grain size of the alloy, where all these factors strongly impact the magnetic properties (Ishikawa and Ohmori, 1990; Zhang *et al.*, 2013). Nanocrystalline $\text{Co}_{76}\text{Zr}_{18}\text{B}_3\text{Si}_3$ ribbons having high M_s of 60 emu/g ($60 \text{ Am}^2 \text{ kg}^{-1}$), H_c of 6.7 kOe (533 kA m^{-1}) and containing grains with size range from 100 to 500 nm, were synthesized by Gao *et al.* (1990) using melt spinning method. It was found that the element substitution was effective in enhancing the H_c , such as the substitution of C and B in Zr-Co alloys increased the saturated magnetization and H_c , respectively, up to a concentration of 2 at% (Ishikawa and Ohmori, 1990; Saito *et al.*, 2005). The substitution of Ti and Si also improved the coercivity

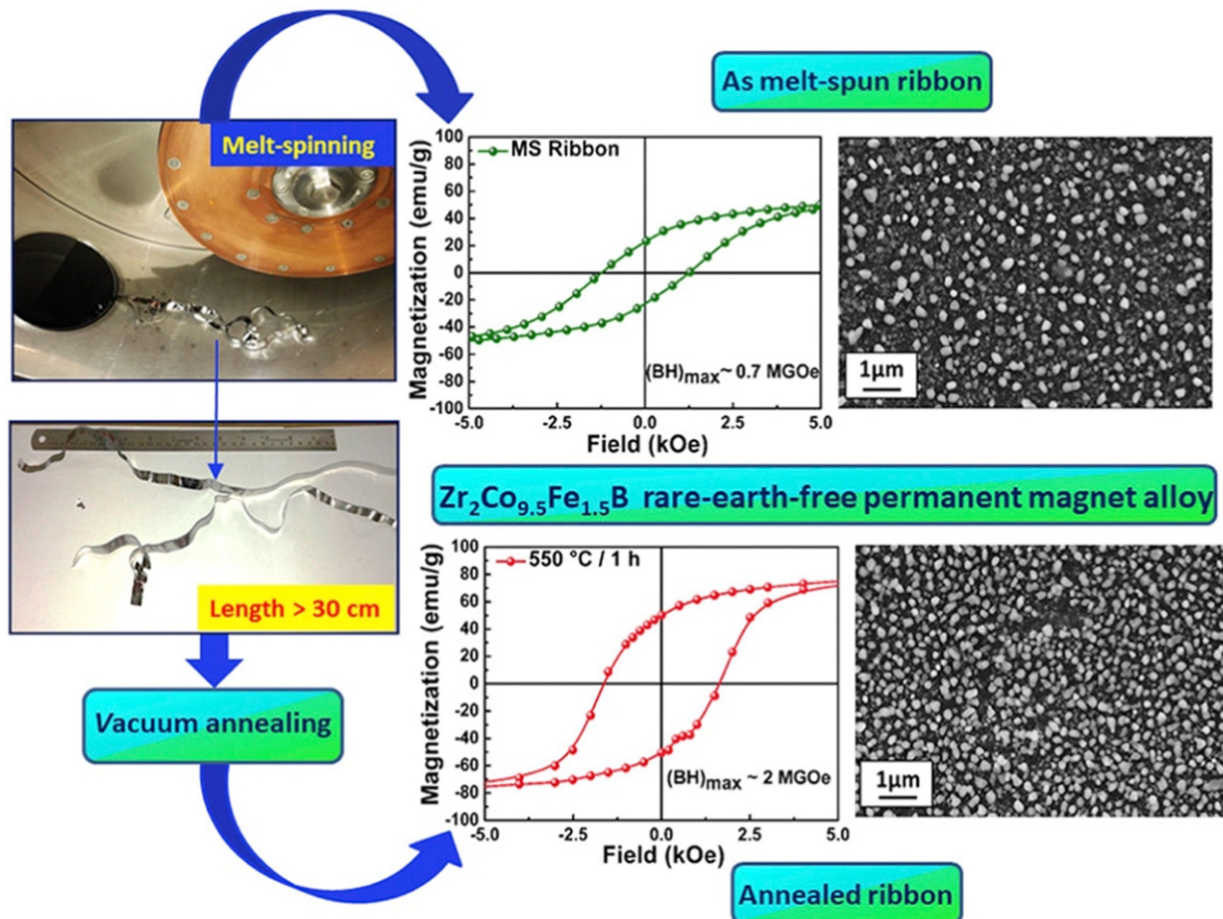


Fig. 4 As melt-spun and annealed $\text{Zr}_2\text{Co}_{9.5}\text{Fe}_{1.5}\text{B}$ ribbons synthesized by rapid solidification method. Graphical abstract in Christopher, N., Anand, K., Singh, N., 2021. Enhancement of hard magnetic properties in rapidly quenched Zr–Co–Fe–B ribbons through vacuum annealing. *Solid Stat. Commun.* 323, 114118.

H_c to a value of 4 kOe (318 kA m^{-1}) (Zhang *et al.*, 2014). The structural and magnetic properties of Mo doped $\text{Zr}_{16}\text{Co}_{84-x}\text{Mo}_x$ nanocrystalline ribbons were investigated by Jin *et al.* (2014). Substitution of Mo supports the formation of $\text{Zr}_2\text{Co}_{11}$ phase, increases its volume fraction, leads to a more refined grain size, and increases the H_c up to 1.5 at% of Mo. A magnetic coercivity H_c value of 2.9 kOe (230 kA m^{-1}) with a $(\text{BH})_{\text{max}}$ value of 4.2 MGOe (33.6 kJ m^{-3}) has been obtained in a selective composition of $\text{Zr}_{16}\text{Co}_{82.5}\text{Mo}_{1.5}$ nanocrystalline ribbon. The co-substitution of small concentration B and Si results in an enhancement of H_c to 4.5 kOe (358 kA m^{-1}) with $(\text{BH})_{\text{max}}$ of 5.3 MGOe (33.6 kJ m^{-3}) for a composition of $\text{Co}_{80}\text{Zr}_{17}\text{Si}_1\text{B}_2$ having a refinement grain size of 10–30 nm (Chang *et al.*, 2013). The substitution of Mo in $\text{Zr}_{16}\text{Co}_{73}\text{Mo}_5\text{Si}_3\text{B}_3$ nanocrystalline ribbons further enhanced the H_c up to 7.9 kOe (629 kA m^{-1}) (Zhang *et al.*, 2012). The analysis of Mo substitution together with Si and B structure indicates that the formation of Co is limited, and the microstructure is refined, which led to an increase of the H_c in the samples. Balamurugan *et al.* (2013) reported the synthesis of $\text{Zr}_2\text{Co}_{11}$ nanofilms using the cluster-deposition method to achieve high H_c and magnetization. This method permitted the direct ordering of high-anisotropy rhombohedral-structure nanoparticles without the high-temperature annealing and alignment of the easy axes before the deposition. These authors obtained high M_r/M_s ratio of 0.88 and H_c of about 4.5 kOe (358 kA m^{-1}) at room temperature with $(\text{BH})_{\text{max}}$ of 16.6 MGOe (132 kJ m^{-3}) for $\text{Zr}_2\text{Co}_{11}$ nanoparticle films. A co-deposition of the high saturation magnetization soft Fe-Co phase was carried out to obtain exchange-coupled nanocomposites. By fabricating $\text{Zr}_2\text{Co}_{11}/\text{Fe-Co}$ nanocomposite film containing 15 vol% Fe-Co soft phase, the $(\text{BH})_{\text{max}}$ is enhanced to 19.5 MGOe (155.2 kJ m^{-3}) due to the exchange-coupling interaction. Although $\text{Zr}_2\text{Co}_{11}$ nanofilms with high $(\text{BH})_{\text{max}}$ were prepared by cluster deposition, a chemical route could be a possible method to prepare $\text{Zr}_2\text{Co}_{11}$ nanoparticles in large quantities enough for bulk magnets synthesis. Very recently, the nanostructured $\text{Zr}_2\text{Co}_{9.5}\text{Fe}_{1.5}\text{B}$ ribbons synthesized by the rapid solidification method were studied in the effects of annealing (Fig. 4) (Christopher *et al.*, 2021). The rhombohedral $\text{Co}_{5.1}\text{Zr}$ hard magnetic phase was formed under optimized vacuum annealing and an increase in magnetic energy product $(\text{BH})_{\text{max}} \sim 2 \text{ MGOe}$ (15.9 kJ m^{-3}) from the value of an as-prepared sample having 0.7 MGOe (5.6 kJ m^{-3}), then those ribbons could be applied as rare-earth-free permanent magnet materials.

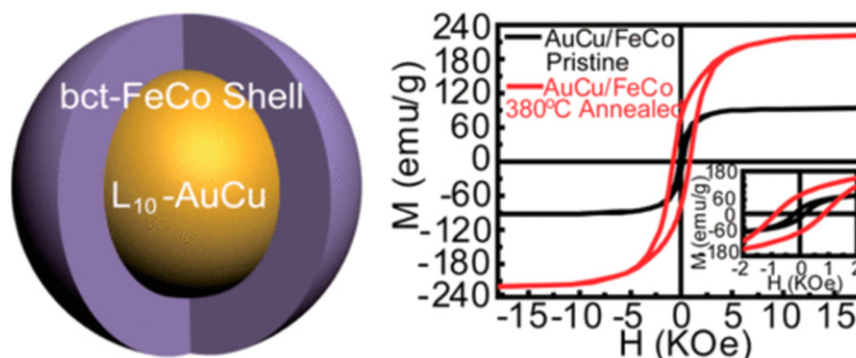


Fig. 5 The AuCu/FeCo (core/shell) structure with the shell of tetragonal FeCo magnet was formed by the L_{10} ordering of the AuCu core with size of 10 nm, having a high coercivity of 846 Oe (673 kA m^{-1}) and saturation magnetization of 221 emu/g ($221 \text{ Am}^2 \text{ kg}^{-1}$). Graphical abstract in Gong, M., Kirkeminde, A., Wuttig, M., Ren, S., 2014. Phase transformation-induced tetragonal FeCo nanostructures. *Nano Lett.* 14, 6493–6498.

Carbides

The Co_2C and Co_3C nanoparticles with a coercivity of 3.4 kOe (270.6 kA m^{-1}) prepared by wet-chemical technique have attracted much attention (Harris *et al.*, 2010; Zhang *et al.*, 2011; Zamanpour *et al.*, 2014; El-Gendy *et al.*, 2014). Providing a suitable control over composition, size, shape, and structure, a polyol reduction offers high yields of nanoparticles, which often exist as a mixture of Co_2C and Co_3C with orthorhombic structure (Harris *et al.*, 2010; Zhang *et al.*, 2011). Their coercivity and saturation magnetization are strongly affected by the volume ratio of Co_3C and Co_2C (Harris *et al.*, 2010). By increasing the fraction of Co_3C , the Co_3C phase with higher magnetocrystalline anisotropy than the Co_2C phase will enhance the coercivity. An enhanced anisotropy constant of 0.75 MJ m^{-3} was observed in $\sim 8.1 \text{ nm}$ size single-phase Co_3C nanoparticles with a high blocking temperature of 571 K (El-Gendy *et al.*, 2014). The first-principle calculations also supported this result, claiming that the cobalt carbide nanoparticles comprise cobalt layers separated by carbon atoms. Furthermore, the cobalt carbide phases are stable up to above 700 K, when the operating temperature of the permanent magnet for most applications is required below 453 K, making them to be a good candidate for permanent magnet-based applications.

Fe-Based Hard Magnets

FeCo magnet

The attractive FeCo alloy is a popular magnetic material among transition metal alloys due to its high saturation magnetization M_s with high Curie temperature T_C (Osaka *et al.*, 1998). Although FeCo alloys usually have low coercivity and small magnetocrystalline anisotropy, tetragonal distorted FeCo alloys are hard magnets exhibiting high coercivity (Cui *et al.*, 2018). A large magnetocrystalline anisotropy and saturation magnetization can be observed in body-centered-tetragonal (bct) FeCo alloys as indicated through the theoretical approach (Wu *et al.*, 2008). In 2006, the magnetic anisotropy induced by Co and Fe films grown on Pd(001) substrate reported by Winkelmann *et al.* showed the possibility of observing high magnetocrystalline anisotropy in tetragonal crystal structure FeCo alloys by straining pure metal films on a substrate (Winkelmann *et al.*, 2006). The formation of tetragonal FeCo can be promoted in an appropriate ratio c/a of lattice-parameter between 1.18 and 1.31, which was proved by Warnicke *et al.* (2007), providing a potential route to earn high magnetocrystalline anisotropy. In 2012, the $(BH)_{\text{max}}$ of FeCo/FePt (001) exchange-spring magnet system was calculated to reach the value of 66 MGOe (525 kJ m^{-3}) and the maximum coercivity is 188 kOe (14965 kA m^{-1}) (Kim and Hong, 2012). In 2015, a $(BH)_{\text{max}}$ of up to 50 MGOe (398 kJ m^{-3}) was observed in an FeCo ultrathin layer strained on a L_{10} FePt film by Giannopoulos *et al.* (2015). These results clearly indicate the potential role of FeCo alloys in R-free permanent magnets. In 2014, the interstitial boron doped FeCo showed that magnetocrystalline anisotropy can attain 0.8 MJ m^{-3} with a $(BH)_{\text{max}}$ of 100 MGOe (796 kJ m^{-3}) (Khan and Hong, 2014).

The syntheses of tetragonal FeCo magnets were carried out under a high temperature and oxygen-free conditions. The size of FeCo particles inevitably increases with increasing temperature and the coercivity can decrease with a large FeCo particles. The particle size controlling has been utilized by introducing an AuCu/FeCo (core/shell) structure (Fig. 5) (Gong *et al.*, 2014). These authors reported that a tetragonal FeCo magnet was formed by the L_{10} ordering of the AuCu core with a size of 10 nm, having a high coercivity of 846 Oe (673 kA m^{-1}) and magnetization of 221 emu/g ($221 \text{ Am}^2 \text{ kg}^{-1}$).

FePt and FePd

Precious metal FePd and FePt alloys magnets with the L_{10} ordered phase have shown an attractive magnetocrystalline anisotropy (Lewis and Jimenez-Villacorta, 2013). The hard magnetic properties of FePt nanostructure are attributed to the presence of a L_{10} face-centered-tetragonal (fct) structure of FePt. FePt in the face-centered-cubic (fcc) disorder phase, can be transformed into the fct order phase with a large magnetocrystalline anisotropy during a high temperature thermal annealing (Bonder *et al.*, 2006; Hai *et al.*, 2003). During the past decades, many synthetic routes have been developed to obtain the L_{10} FePt alloys, such as exchange-coupled assembly, one-step thermal route with metal precursors, and microemulsion. In 2003, the transition of the fct structure of

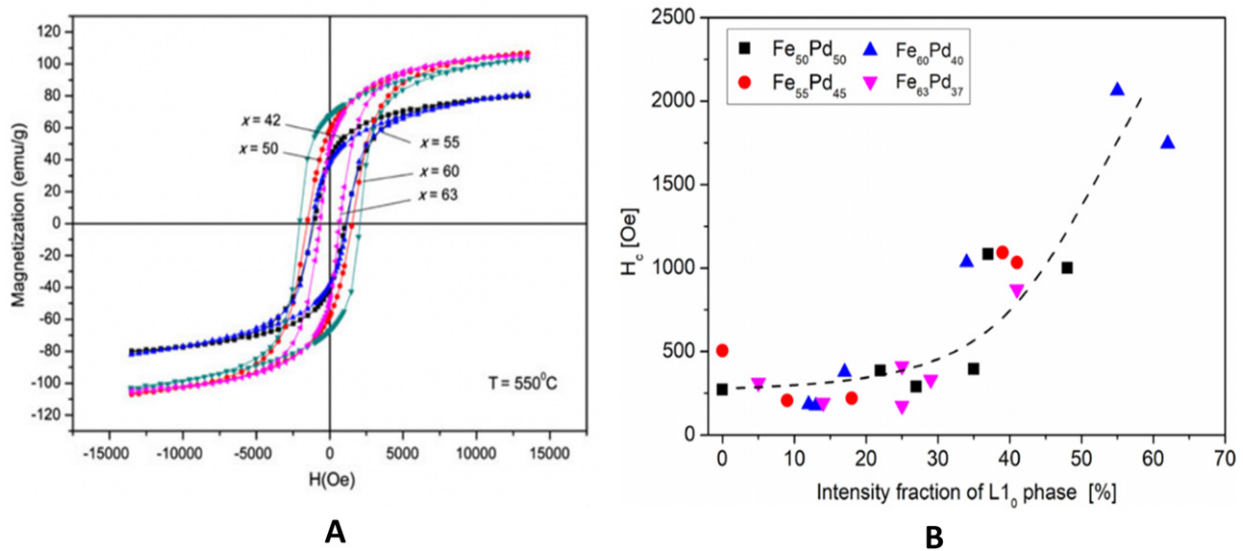


Fig. 6 (A) Magnetic hysteresis loops of FePd nanoparticles prepared by sonochemistry method in various compositions annealed at 550°C . (B) Coercivity H_c as a function of intensity fraction of L_{10} phase in FePd nanoparticles synthesized by sonoelectrodeposition method in various compositions. Reproduced from (A) Van, N.T.T., Trung, T.T., Nam, N.H., *et al.*, 2013. Hard magnetic properties of FePd nanoparticles. *Eur. Phys. J. Appl. Phys.* 64, 10403. (B) Luong, N.H., Trung, T.T., Hong, T.T., *et al.*, 2022. Relating the magnetic coercivity to the L_{10} ordered FePd phase in annealed $\text{Fe}_x\text{Pd}_{100-x}$ nanoparticles. *Appl. Phys. A* 128, 936

FePt, with a coercivity of 1.7 kOe (135.3 kA m^{-1}) at 10K, was achieved by a chemical route (Jeyadevan *et al.*, 2003). Monodisperse FePt nanoparticles were successfully synthesized by Sun *et al.* (2000) through the reaction of iron pentacarbonyl and platinum acetylacetonate in the presence of oleylamine and oleic acid. Sun *et al.* (2003) also reported fct-FePt nanoparticles with a high coercivity of 7.6 kOe (605 kA m^{-1}) synthesized by a chemical reaction route, which were the common preparation routes in the past decades. However, the aggregation of FePt nanoparticles upon thermal annealing is still a long-lasting challenge. In 2004, the synthesis of FePt nanoparticles with an average diameter of 6 nm and a coercivity reaching 13 kOe (1035 kA m^{-1}) at room temperature was reported by Chen *et al.* (2004). The transition from the disordered fcc phase to the ordered fct phase occurred at temperatures above 650°C , while the morphology and structure of FePt nanoparticles were strongly influenced by the sintering process at high temperatures. In 2019, the eutectic melt crystallization of ordered L_{10} -FePt was developed to synthesize an fct FePt alloy with a coercivity of 16 kOe (1274 kA m^{-1}), a saturated magnetization of 33.6 emu/g ($33.6 \text{ Am}^2 \text{ kg}^{-1}$) and the maximum energy product of 5 MGOe (39.8 kJ m^{-3}) (Zhang *et al.*, 2019; Shao and Ren, 2020). In parallel, a simple chemical-physical route of electro-sonochemistry was developed to synthesize the L_{10} FePt nanoparticles within the annealing temperature range of 450 – 700°C , but the aggregation of nanoparticles during the high temperature annealing is still a remaining issue (Nam *et al.*, 2012). Two-phase hard L_{10} -ordered FePt and soft iron-rich fcc Fe-Pt nanostructures were investigated by Liu *et al.* (2011b). The largest values of M_s , H_c , and $(BH)_{\text{max}}$ obtained in their samples are 1287 emu/cm^3 (1.616 T), 51 kOe (4059.6 kA m^{-1}), and 54 MGOe (429.8 kJ m^{-3}), respectively. These authors pointed out that a factor contributing to the high coercivity and energy product of their nanostructured Fe-Pt is isolation between different two-phase nanostructures, which suppresses the macroscopic expansion of magnetic domain walls.

Besides FePt, iron palladium (FePd) alloys have attracted much interest due to their high magnetocrystalline anisotropy and energy density, although these values are lower than those of FePt (Tanaka *et al.*, 2001). Among the synthesis routes of FePd nanoparticles, the colloidal solution is one of the most studied approaches. Similar to FePt, the order of fct FePd by annealing is the origin of hard magnetic properties, and the size of annealed FePd nanoparticles also cannot always be controlled during the sintering process (Kirkemide and Ren, 2014; Liu, 2009). The reduction of palladium acetylacetonate and thermal decomposition of iron pentacarbonyl operated in a three-neck flask resulted in the $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles with a magnetic coercivity of 685 Oe (54.5 kA m^{-1}) and the ordering parameter S was obtained using lattice parameters measured by the X-ray diffraction (Chen and Nikles, 2002). FePd prepared by Chen and Nikles did not transform to the L_{10} phase after annealing at a sufficiently high temperature of 700°C for 3 h (Chen and Nikles, 2002). FePd nanoparticles fabricated by an electron-beam evaporation technique were reported to have a coercivity value of 1.2 kOe (95.5 kA m^{-1}) after annealing at 773K for 1 h (Sato and Hirotsu, 2006; Sato *et al.*, 2000). In 2004, monodisperse FePd nanoparticles with an average size of 13.5 nm and controlled by surfactants were reported to show a coercivity of 350 Oe (279 kA m^{-1}) (Hou *et al.*, 2004). In 2013, L_{10} -FePd-Fe nanocomposite prepared by a one-pot synthesis, which was tailored by a stable thermal mixture, showed a coercivity of 2.6 kOe (207 kA m^{-1}) and a saturation magnetization of 190 emu/g ($190 \text{ Am}^2 \text{ kg}^{-1}$) (Yu *et al.*, 2013). Meanwhile, the sonochemistry and electro-sonochemistry methods were introduced to synthesize FePd nanoparticles with a coercivity of 2.1 kOe (167.2 kA m^{-1}) at room temperature (Fig. 6) (Van *et al.*, 2013; Luong *et al.*, 2017, 2022). The magnetic properties with respect to the dependence of the nanostructure, the

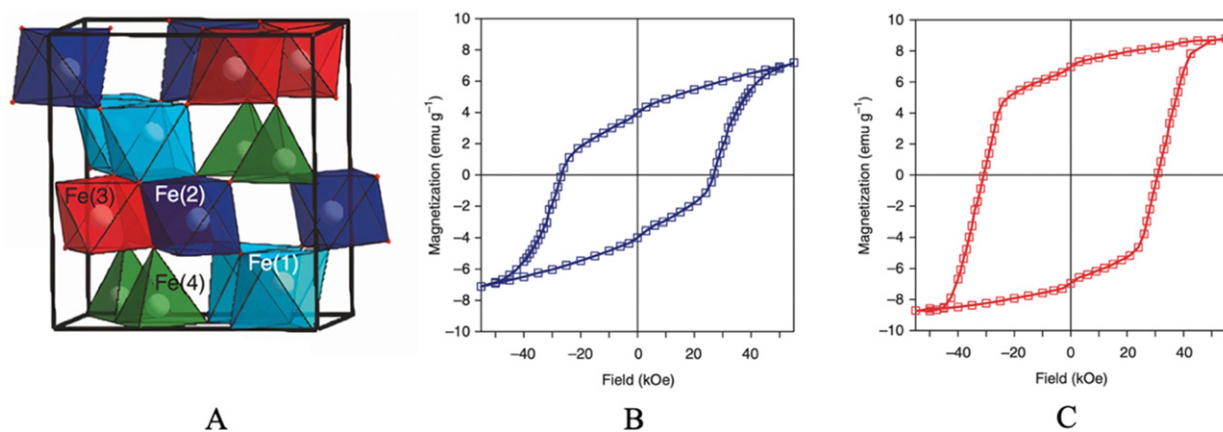


Fig. 7 (A) Scheme of ϵ - Fe_2O_3 structure. Room-temperature magnetic hysteresis loops of non-oriented (B) and oriented (C) ϵ - Fe_2O_3 nanoparticles doped with Rh. Reproduced from (A) Sans, J.A., Monteseguro, V., Garbarino G., *et al.*, 2018. Stability and nature of the volume collapse of ϵ - Fe_2O_3 under extreme conditions. *Nat. Commun.* 9, 4554. (B) and (C) Namai, A., Yoshikiyo, M., Yamada, K., *et al.*, 2012. Hard magnetic ferrite with a gigantic coercivity and high frequency millimetre wave rotation. *Nat. Commun.* 3, 1035.

morphology, and the composition of nanoparticles, were investigated under the effect of the annealing in the temperature range of 450–700°C. The correlation between the magnetic coercivity and the L_{10} ordered FePd phase fraction has been established for the $\text{Fe}_x\text{Pd}_{100-x}$ nanosystem. In 2020, a eutectic crystallization method was introduced to synthesize FePd nanoparticles with an average size of 50 nm, a high coercivity of 1.8 kOe (143.3 kA m⁻¹) and a magnetization of 17 emu/g (17 Am² kg⁻¹) (Shao *et al.*, 2020; Shao and Ren, 2020). This method can reduce the aggregation induced by high temperature annealing of magnetic nanoparticles and simplify the preparation process of FePd magnets.

ϵ - Fe_2O_3

Among different existing crystalline iron oxides of α -, β -, γ -, and ϵ - Fe_2O_3 , ϵ - Fe_2O_3 has attracted much interest due to its hard magnetic properties (Sivkov *et al.*, 2016; Sans *et al.*, 2018). They exhibit as potential candidates for applications in microwave and recording media, since the ϵ - Fe_2O_3 phase is formed under the conditions with exclusively high temperature. In the past decades, the most common synthesis method is a silica matrix route, depending on the chemical reaction. For instance, nanocrystals ϵ - Fe_2O_3 with rod-like morphology in sizes of 100–140 nm long and 20–40 nm wide were synthesized in a silica matrix and showed a large coercivity of 20 kOe (1592 kA m⁻¹) at room temperature (Jin *et al.*, 2004). In 2008, an advanced route combining the reverse-micelle and sol-gel methods was introduced to synthesize ϵ - Fe_2O_3 nanowires with an average size of 7 nm (Sakurai *et al.*, 2008). In 2012, a chemical synthesis in a silica matrix was reported to produce nanocrystalline ϵ - Fe_2O_3 with a giant coercivity value of 31 kOe (2467.6 kA m⁻¹), which is in comparable to that of R magnets (Fig. 7) (Namai *et al.*, 2012). A significant improvement of magnetic properties with the highest coercivity of 45 kOe (3582 kA m⁻¹) at 200K and 35 kOe (2786 kA m⁻¹) at 300K for ϵ - Fe_2O_3 film was achieved when the film was prepared from metal instead of iron ions (Ohkoshi *et al.*, 2017). The fabrication of high phase purity nanoscale ϵ - Fe_2O_3 , which can improve the magnetic parameters, is still a technical challenge (Cleron *et al.*, 2022).

Fe_{16}N_2 hard magnet

The thermal stability and the synthesis of bulk α'' - Fe_{16}N_2 , one of the promising permanent magnet candidates due to their large magnetocrystalline anisotropy of $K_1 \sim 10^7$ erg cm⁻³ (1.0 MJ m⁻³) and a giant saturation magnetization of ~ 234 emu/g though unfortunately thermally unstable, were quantitatively studied and reported (Ogawa *et al.*, 2013; Yamamoto *et al.*, 2013; Jack, 1995). Due to its superior magnetic properties, many studies were carried out on different types of α'' - Fe_{16}N_2 , such as thin films and nanoparticles. For example, α'' - Fe_{16}N_2 nanoparticles were prepared using precursors containing Fe_2O_3 in NH_3 - H_2 mixed gas (Bao *et al.*, 1994). Various synthesis routes were reported, but these routes usually produced multiple phases, including α'' - Fe_{16}N_2 , which influenced the magnetic properties. Jiang *et al.* reported the preparation of α'' - Fe_{16}N_2 by ball milling and shock compaction approach, obtaining a large coercivity of 854 Oe (68 kA m⁻¹) and a high saturation magnetization of 210 emu/g (210 Am² kg⁻¹) (Jiang *et al.*, 2016). The value of the maximum magnetic energy product $(\text{BH})_{\text{max}}$ of α'' - Fe_{16}N_2 can reach ~ 20 MGOe (159.2 kJ m⁻³) at room temperature, showing the potential applications in permanent magnets. Recently, a low-temperature nitriding process was reported in the synthesis of α'' - Fe_{16}N_2 nanoparticles with a high α'' - Fe_{16}N_2 volume ratio of up to 93% achieving the coercivity of 2.0 kOe (159.2 kA m⁻¹) and the saturation magnetization of 178 emu/g (178 Am² kg⁻¹) at room temperature (Ma *et al.*, 2020).

FeNi magnet

Pauleve *et al.* synthesized the L_{10} -FeNi phase, one of the rare-earth-free magnet candidates, by neutron irradiation under a magnetic field (Pauleve *et al.*, 1962). The order-disorder transition temperature of the L_{10} -FeNi phase, known as tetrataenite, is shown to be 593K. In 1989, this transition temperature is further demonstrated by Reuter *et al.* using electron irradiation (Reuter *et al.*, 1989).

Table 1 Magnetic properties of some representative hard magnetic materials. H_c , M_s , and $(BH)_{\max}$ are room-temperature values

Materials	Structure/Form	H_c (kA m ⁻¹)	M_s	$(BH)_{\max}$ (kJ m ⁻³)	T_c (°C)	References
SmCo ₅	Nanoparticles	5731	90 Am ² kg ⁻¹	–	747 ^a	Dong <i>et al.</i> (2019)
SmCo ₅	Nanocomposite	–	–	152.8	–	Rong <i>et al.</i> (2010)
Nd-Fe-B	Nanostructured magnet	1004	1.574 T	400	315 ^b	Liu <i>et al.</i> (2010)
Alnico 9	Nanostructures	119.4	2.39 T	71.64	770	Zhou <i>et al.</i> (2014)
CoFe ₂ O ₄ /SrFe ₁₂ O ₁₉ ferrite	Nanocomposite	182.2	62.8 Am ² kg ⁻¹	17.5	–	Pan <i>et al.</i> (2015)
Mn ₅₀ Bi ₄₅ Mg ₃ In _{0.5} Sb _{1.5}	Melt-spun	676.6	–	92.3	–	Gabay <i>et al.</i> (2020)
τ -MnAl	Thin films	851.7	0.454 T	35.34	–	Nie <i>et al.</i> (2013)
L1 ₀ -Mn _{1.5} Ga	Films	3407	0.34 T	20.7	–	Zhu <i>et al.</i> (2012)
Mn ₅ Si ₃	Nanoparticles	71.6	1.007 T	–	317	Das <i>et al.</i> (2016)
Zr ₂ Co ₁₁	Nanostructures	358	1.02 T	132	510	Balamurugan <i>et al.</i> (2013, 2014)
Co ₂ C/Co ₃ C	Nanocomposite	270.6	73 Am ² kg ⁻¹	20.7	237	Harris <i>et al.</i> (2010)
Fe ₄₅ Co ₅₅ /FePt	Thin films	–	1.884 T	398	–	Giannopoulos <i>et al.</i> (2015)
L1 ₀ /fcc FePt	Nanocomposite	4059.6	1.616 T	429.8	477 ^c	Liu <i>et al.</i> , (2011)
L1 ₀ -FePd-Fe	Nanocomposite	207	190 Am ² kg ⁻¹	–	–	Yu <i>et al.</i> (2013)
ε -Rh _{0.14} Fe _{1.86} O ₃	Films	2786	13.4 Am ² kg ⁻¹	–	–	Ohkoshi <i>et al.</i> (2017)
α'' -Fe ₁₆ N ₂	Nanoparticles	159.2	178 Am ² kg ⁻¹	–	–	Ma <i>et al.</i> (2020)
FeNi	Nanostructures	79.6	122 Am ² kg ⁻¹	–	–	Gong and Ren (2015)
Fe ₃ Se ₄	Nanostructures	318.4	–	–	47	Zhang <i>et al.</i> (2011)

^aValue for compound.^bValue for Nd₂Fe₁₄B compound (Coey, 2020).^cValue for FePt compound (Coey, 2011).

Usually, L1₀-FeNi is only found naturally in meteorites due to the long-time of more than 10,000 years at 573K taken for an atomic jump of nickel in FeNi alloys (Kojima *et al.*, 2012; Mohapatra and Liu, 2018). In 2015, the magnetic properties of tetragonal L1₀-FeNi obtained from the meteorite NWA 6259 from Northwest Africa were reported with a large anisotropy of 14.4 kOe (Poirier *et al.*, 2015). In 2016, tetragonal FeNi was formed by an annealing and the cubic - tetragonal structure transition of the FeNi lattice was observed (Montes-Arango *et al.*, 2015). Meanwhile, the L1₀-FeNi powder prepared by a chemical synthesis of reductive reaction, showed a magnetic coercivity of 220 kA m⁻¹ (2765 Oe) (Hayashi *et al.*, 2013). However, the tetragonal FeNi alloys are normally unstable, and a rational epitaxial core/shell nanostructure was designed to stabilize tetragonal FeNi nanocrystals, where the reconstruction of tetragonal FeNi was activated by the surface stress with the existence of AuCu cores (Gong and Ren, 2015). The designed FeNi crystals showed a magnetic coercivity of ~1.0 kOe (79.6 kA m⁻¹) and a saturated magnetization of 122 emu/g (122 Am² kg⁻¹).

Fe₃Se₄ magnet

The NiAs-type structure Fe₃Se₄ nanocrystal has attracted interest due to its hard magnetic properties (Bishwas *et al.*, 2014). In principle, Hirakawa suggested that the single crystal of Fe₃Se₄ can be magnetized in the *c*-plane (Hirakawa, 1957), and the energy product of Fe₃Se₄ increased up to 0.12 MGOe (0.955 kJ m⁻³) was reported (Bishwas *et al.*, 2014). In order to improve magnetic properties, the synthesis of Mn doped Fe₃Se₄ nanostructures has been introduced. For example, Fe₃Se₄ nanostructures were synthesized by organic-solution-phase chemical decomposition and exhibited a high coercivity of 40 kOe (3184 kA m⁻¹) at 10K and 4.0 kOe (318.4 kA m⁻¹) at room temperature (Zhang *et al.*, 2011; Long *et al.*, 2011). Although getting intense interest, more advanced routes aiming to improve the generation of Fe₃Se₄ nanostructures and their magnetic properties are still needed, which also represent a challenging task (Li *et al.*, 2019).

Conclusion and Perspectives

This chapter reviews recent developments in hard magnetic nanostructured materials. Table 1 summarizes the magnetic properties of some representative hard magnetic materials. Nanostructuring is of help to improve the overall hard magnetic properties of the materials. The progress made in the last years on the study of these materials gives promise for their future wider applications. It is anticipated that research on this important group of materials will be continuing with greater intensity. The extension of the materials list will be one of the trends in hard magnetic nanostructured materials research in years to come.

Acknowledgment

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